LONG-TERM *IN VITRO* FLUORIDE RELEASE AND RE-RELEASE FROM ORTHODONTIC BONDING MATERIALS CONTAINING FLUORIDE

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Long-Term *In Vitro* Fluoride Release and Re-release from Orthodontic Bonding Materials Containing Fluoride

BY

Warren Jason Cohen, D.D.S.

A Thesis/Practicum submitted to the Faculty of Graduate Studies

of the University of Manitoba

in partial fulfilment of the requirements for the degree

of

Master of Science

Abstract

The objectives of this study were to compare *in vitro* long-term (30 month) fluoride release rates and re-release rates (following fluoride exposure) from three orthodontic bonding materials containing fluoride using a disc model, and to compare the fluoride release rates of two orthodontic bonding materials containing fluoride using an *in vitro* tooth-bracket model. For part I of the study, 10 samples of each material (Python™, TP Orthodontics, Laporte, IN; Assure™, Reliance Orthodontic Products Inc., Itasca, IL; Fuji Ortho™ LC, GC America Inc., Central Islip, NY; and Transbond™ XT, 3M Unitek, Monrovia, CA) were fabricated and stored in de-ionized distilled water at 37°C. Five samples had fluoride release rates measured at days 546, 637, 730, 821 and 913 from time of initial fabrication, while 5 samples were exposed to fluoride (Nupro 2% NaF gel, Dentsply Canada, Woodbridge, ON) for 4 minutes at day 535 and had measurements taken on days 546, 548, 552, 575, 637, 730, 821 and 913. To prevent cumulative measurements, the storage solutions were changed 24 hours prior to measurement. For part II of the study, 10 samples of each material (Assure™ and Quick Cure™, Reliance Orthodontic Products Inc., Itasca, IL; and Transbond™ XT) were used to bond orthodontic brackets to extracted human premolars and stored as in part I. Measurements of fluoride release were taken on days 1, 3, 7, 30, 90 and 180. For part I, statistically significant differences were found in fluoride release rates ($p<0.0001$), with Fuji Ortho LC releasing the most fluoride, followed by Python and Assure at all time points in the non-fluoride exposed group. In the group exposed to fluoride there were significant differences in fluoride release ($p<0.0001$), with Fuji Ortho LC releasing the most fluoride. A "burst-effect" pattern of fluoride release was seen following fluoride exposure for all materials.

In part II, Assure released significantly greater levels of fluoride on day 1, and clinically significant levels of fluoride up to day 30. It was concluded that Fuji Ortho™ LC, Assure™ and Python™ have sufficient long-term fluoride release rates to reduce white spot formation and all are recommended as suitable orthodontic bonding materials.

Dedication

This thesis is dedicated to my
parents Leon and Sharon,
grandmother Annie Kustan,
brother Harvey,
and all my family and friends who supported
me throughout my academic experience.

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I would like to express my sincere appreciation and gratitude to the following people for making this project possible:

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Chapter 1

Introduction

1.1 Foreword

As orthodontic treatment is a very common procedure, it is critical to minimize any associated complications. This is a particular concern for orthodontics as the occurrence of enamel demineralization is a significant problem related to the placement of fixed orthodontic appliances (Gorelick *et al.*, 1982; Øgaard, 1989; Thilander, 1992).

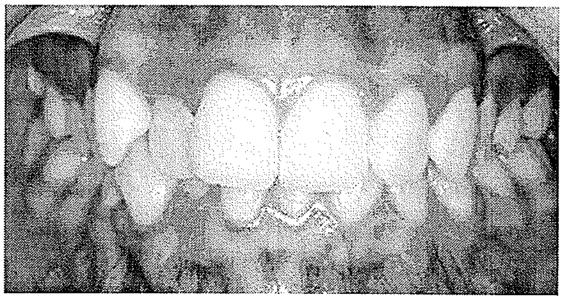


Figure 1: Pre-orthodontic treatment

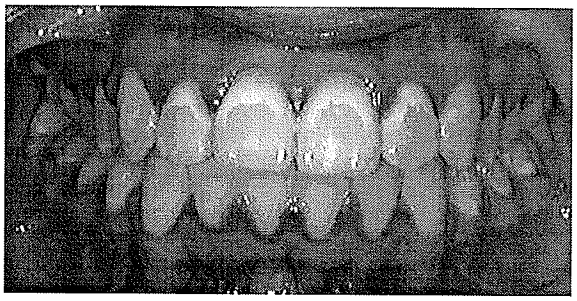


Figure 2: Post-orthodontic treatment showing enamel decalcification

Finding methods of reducing such iatrogenic decalcification following orthodontic treatment is imperative and centers on attempts to develop bonding adhesives that release fluoride. Valk and Davidson (1987) reported that bonding with glass-ionomer cement provided protection for a 1 mm area around brackets. As glass-ionomer cements have low bond strengths (Fricker, 1994), modifications to both glass-ionomer cements and composite resins have produced "hybrid" bonding materials with fluoride release and improved bond strengths (5% bond failure of resin-modified glass ionomer cement vs. 8.3% for composite resin). Chadwick and Gordon (1995) found higher fluoride concentrations in biopsies of enamel bonded with Vitrebond®, a resin-modified glass-ionomer material, as compared with initial biopsy measurements.

Polyacid-modified composite resins have been modified through the addition of polyacids and/or fluoride-containing ground glass, which Ashcraft *et al.* (1997) found to release less fluoride than resin-modified glass-ionomer materials. Such modifications have created a continuum of materials purported to release fluoride where "hybrid" bonding materials take up and release fluoride from the oral environment (Ashcraft *et al.*, 1997).

1.2 Motivation for the Study

It is important to determine which materials release the amount of fluoride required to provide clinically significant caries inhibition (Rawls, 1987) using different *in vitro* models since the amount of fluoride released varies with the *in vitro* model (Monteith *et al.*, 1999). This study investigated three materials - Python™ (TP Orthodontics); Assure™ (Reliance Orthodontic Products Inc.); and Fuji Ortho™ LC (GC America Inc.), and two *in vitro* models – disc and tooth-bracket samples. This investigation partly served as a continuation of a previous study (McNeill, 2000), to provide information on the fluoride release patterns of these materials.

1.3 Purpose of the Study

The aims of this study were threefold:

1) To compare the long-term (30 month) fluoride release rates *in vitro* from discs of two recently marketed polyacid-modified composite resins - Python™ (TP Orthodontics) and Assure™ (Reliance Orthodontic Products Inc.) with that from a resin-modified glass-ionomer (Fuji Ortho™ LC - GC America Inc.) and with a non-fluoride-containing composite resin (Transbond™ XT - 3M Unitek) serving as a control. The interest was to provide a long-term continuation of a previous short-term study (McNeill, 2000), which ended at the 6-month evaluation point.
2) To assess the capability of Python™, Assure™ and Fuji Ortho™ LC to imbibe and re-release fluoride compared with a non-fluoride-containing composite resin (Transbond™ XT) as a control.
3) To compare the fluoride release rates from Assure™ and Quick Cure™ (Reliance Orthodontic Products, Inc.) with that from a non-fluoride-containing composite resin (Transbond™ XT - 3M Unitek) as a control using an *in vitro* tooth-bracket model.

1.4 Null Hypothesis

The null hypothesis states:

1) Samples of resin-modified glass-ionomer (Fuji Ortho™ LC) will not release more fluoride than either polyacid-modified composite resin (Assure™ and Python™) or a non-fluoride-containing composite resin (Transbond™ XT).
2) Samples of resin-modified glass-ionomer (Fuji Ortho™ LC) will not imbibe and re-release more fluoride than either polyacid-modified composite resin (Assure™ and Python™) or a non-fluoride-containing composite resin (Transbond™ XT).
3) A tooth-bracket model of either polyacid-modified composite resin (Assure™ and Quick Cure™) will not release more fluoride than a non-fluoride-containing composite resin (Transbond™ XT).

Chapter 2

Review of the Literature

2.1 Enamel Decalcification

2.1.1 The White Spot Lesion

Enamel demineralization involves the loss of phosphate and calcium ions from enamel, leading to increased opacity. Such white spot lesions cover changes that range from very early whitish opaque enamel surface spots to extensive chalky enamel surfaces where small parts may fracture (Fejerskov and Clarkson, 1996).

2.1.2 Enamel Decalcification in Orthodontics

Direct bonding of brackets to enamel is useful because it eliminates the need for orthodontic bands (Proffit 2000), although the downside includes an increased prevalence of enamel demineralization and white spot formation (Gorelick *et al.*, 1982). In their study of 121 patients with bonded orthodontic appliances, 49.6% showed visually determined enamel demineralization of at least one tooth, compared with only 24% of control patients. Of the total teeth examined, only 10.8% showed such lesions, indicating significant variation among patients. As 50% of bonded patients showed no increase in white spot lesion formation, Gorelick *et al.* (1982) suggested that variations in enamel structure, salivary composition, or tooth brushing influenced this process.

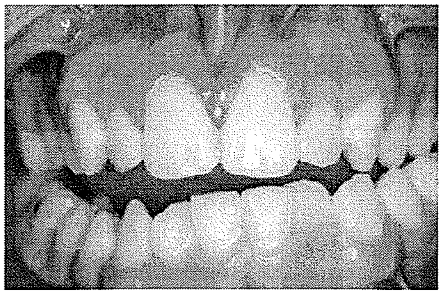


Figure 3: Pre-orthodontic treatment

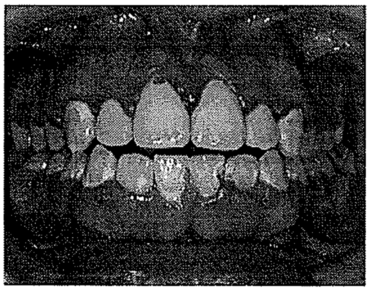


Figure 4: Post-orthodontic treatment showing enamel decalcification and frank cavitation

Øgaard *et al.* (1988) utilized an *in vivo* orthodontic band model to induce caries lesions in premolars planned for extraction, and cemented ill-fitting orthodontic bands to facilitate plaque accumulation on the buccal surfaces. The teeth were extracted after 4 weeks and showed visible white spot lesions in the absence of a fluoride regimen, with mineral loss up to a depth of 100 μm and an intact surface layer.

Øgaard (1989) investigated the prevalence of white spot lesions in 51 patients five years after conclusion of orthodontic treatment. The presence of bonded orthodontic appliances led to significantly more patients with white spot lesions as compared with untreated control subjects (96% of orthodontic patients had white spot lesions, compared with only 85% of control patients). The greatest prevalence of white spot lesions was found on first molars, canines and premolars in the treated group, possibly related to the presence of molar bands or the anatomic shape of teeth necessitating more gingival bracket placement. The authors suggested that the use of fluoride toothpaste and mouth rinses probably lead to a layer of fluorapatite (FAP) sealing the lesion, preventing remineralization and disappearance of the white spots even five years after treatment.

O'Reilly and Featherstone (1987) also demonstrated *in vivo* enamel demineralization around orthodontic brackets after only one month. They performed enamel microhardness testing around orthodontic brackets on 58 teeth extracted one month after bonding. Teeth that were brushed at least once daily with a fluoride-containing dentifrice (1,100 ppm fluoride) showed a significant amount of demineralization immediately adjacent to bonded orthodontic brackets. Microhardness testing revealed that the mineral loss was limited to an area 50 to 75 μm beyond the periphery of the bracket, and was not visible clinically. This is consistent with very early stages of caries lesion formation (surface softening), which normally precedes the formation of a well-mineralized surface layer (O'Reilly and Featherstone, 1987).

2.1.3 Etiology of Enamel Demineralization Around Orthodontic Appliances

Fixed orthodontic appliances alter the ecology of the oral environment by creating areas of stagnation. Normal physical cleansing forces such as movement of food and the oral musculature, as well as the flow of saliva are reduced or prevented, allowing acceleration of plaque accumulation (Chang *et al.*, 1997). This results in a favourable environment that leads to increased levels of *Streptococcus mutans* and lactobacilli (Arneberg *et al.*, 1984; Lundström and Krasse, 1987b; Rosenbloom and Tinanoff, 1991). Plaque from such retentive sites in orthodontic patients varies in pH values and fluoride concentrations, with lower values on maxillary teeth than on mandibular anterior teeth (Arneberg *et al.*, 1997). Thilander (1992) suggested that acid etching of enamel might be a causative factor in enamel white spot formation. However, Gorelick *et al.* (1982) found that the presence of lower lingual bonded retainers resulted in no white spot formation over an average wear time of 24 months in 60 patients, and suggested that the acid application did not, by itself, cause white spot lesions probably because of the protection afforded from free flowing saliva in the lingual area. Since an increased surface for plaque adhesion coupled with poor oral hygiene provides the environment for increased demineralization of tooth surface around the orthodontic bracket base, it is the goal of the orthodontic profession to prevent the occurrence of such iatrogenic damage.

2.2 Fluoride

2.2.1 Effects of Fluoride on Enamel

The cariostatic effect of fluoride is thought to relate to a series of unrelated, yet synergistic effects, arising through application of various concentrations of fluoride at different times (White and Nancollas, 1990; Levine, 1991). Unfortunately, space is limited in this context to expand on the cariostatic mechanisms of fluoride; however many schools of thought prevail regarding the method by which fluoride reduces dental caries (ten Cate and Featherstone, 1996). Levine (1991) believes that pre-eruptive systemic fluoride treatment and fluoride content in enamel is important for providing protection from caries. In summarizing the literature White and Nancollas (1990) found that many authors view the lower solubility and presumed increased fluoride retention of "firmly bound" fluorapatite (FAP) as important in imparting caries resistance. However, Fejerskov *et al.* (1981) feel that use of systemic fluoride treatment during enamel formation is of "limited value". Øgaard *et al.* (1988) used shark enamel to show limited resistance of FAP against caries attacks in an intra-oral human caries model.

The current view is that firmly incorporated fluoride is of less importance than fluoride ion present in oral fluid during de- and remineralization cycles (Fejerskov, 1981; ten Cate and Featherstone, 1996). This view depends on the following observation stated by Fejerskov *et al.* (1981): "Based on our present knowledge obtained from epidemiological studies, clinical trials, microbiological and clinical studies, laboratory experiments and theoretical physico-chemical considerations, considerable evidence is available to substantiate the assertion that fluoride, even in low concentrations, is necessary in the oral fluids to obtain maximum caries inhibition. The relative significance of fluoride bound in the enamel remains uncertain. Therefore continuous or frequent supplementation to oral fluids is mandatory, particularly in cases of increased cariogenic challenge at any age." ten Cate and Featherstone (1996) state that "fluoride acts by inhibiting mineral loss at the crystal surfaces and by enhancing this rebuilding or remineralization of calcium and phosphate in a form more resistant to subsequent attack." Fluoride in solution has greater influence on demineralization and remineralization than do the bulk precipitate forms (CaF_2 and FAP) (Featherstone *et al.*, 1990; White and Nancollas, 1990). However, renewed interest has focused on "loosely bound" CaF_2 as a potential "reservoir" for solution ionic fluoride (White and Nancollas, 1990). CaF_2 provides free fluoride ions as it dissolves and may act as a long-term store for fluoride during periods of de- and remineralization (ten Cate and Featherstone, 1996). In summarizing the literature, White and Nancollas (1990) reported that carious enamel is much more reactive with fluoride than sound enamel, as shown by rapid acquisition of greater amounts of total fluoride. Additionally, acquired fluoride strongly enhances both remineralization and demineralization resistance (White and Nancollas, 1990). Clarkson *et al.* (1988) showed that the progress of carious lesions within enamel is inversely proportional to the fluoride concentration within the lesion, which is in turn dependent on the presence of acquired loosely bound fluoride (CaF_2) in the sound enamel following topical fluoride application.

Much debate has focused on finding the most beneficial method and concentration for supplemental fluoride delivery. Featherstone *et al.* (1990) found an inverse dependence of relative mineral loss on the logarithm of fluoride concentration, or stated in another way, that an increase in fluoride in the treatment solution does not translate directly into a proportionately larger effect. According to their mathematical model, a fluoride concentration of 62 mg/L (or ppm) would provide 80% protection while 178 mg/L would give 90% protection. Rather than simply empirically increasing fluoride dosages, delivery mechanisms are needed that provide relatively low fluoride concentrations for longer time periods. This would allow fluoride to accumulate in plaque fluid and subsequently diffuse between the enamel crystals, enhancing the remineralization process (Featherstone *et al.*, 1990; Margolis and Moreno, 1990; ten Cate and Featherstone, 1996). This provides strong theoretical support for bonding materials that provide continual local fluoride release at the site of demineralization around orthodontic brackets.

2.2.2 Effects of Fluoride on Oral Bacteria

Fluoride has several direct and indirect effects on the bacterial cell, some of which may influence acidogenic bacteria in dental plaque (Hamilton and Bowden, 1996). The uptake of fluoride into bacterial cells during periods of carbohydrate metabolism is facilitated with the permeable form, HF. Once inside the bacterial cell, HF dissociates into H^+ and F^-, each with significant effects (Hamilton and Bowden, 1996). H^+ causes decreased intracellular pH, leading to a less favourable cytoplasmic environment for the function of many enzymes. F^- interacts with various F-sensitive enzymes, causing inhibition of enzymatic activity. This affects many metabolic activities including the glycolytic pathway, sugar transport, proton-extruding ATPases, the proton motive force, macromolecule synthesis and others (Hamilton and Bowden, 1996). Fluoride levels as low as 0.45 μg/mL at pH 5.0 can inhibit lactic acid production of certain strains of *S. mutans* (Harper and Loesche, 1986). However, the minimum inhibitory concentration of fluoride ion in solution required to inhibit demineralization in a solution containing Ca and P at levels found in dental plaque (Moreno and Margolis, 1988) is estimated at 1 to 2 ppm (or possibly higher *in vivo*). If the fluoride concentration in plaque rises above the minimum inhibitory concentration, the enamel becomes insoluble and the antimicrobial effects of fluoride become less significant (Van Loveren, 1990).

2.2.3 Topical Fluoride Application and White Spot Prevention

Fluoride rinsing programs can help to reduce white spot formation (Geiger *et al.*, 1992). Their protocol involved rinsing with 10 ml of 0.05% sodium fluoride daily before bedtime after brushing with fluoride-containing toothpaste (for 9 to 49 months depending on treatment time). They showed significant reduction in white spot formation in patients compliant with a fluoride rinsing protocol (21% of patients with white spots) compared with non-compliant patients (49% showed white spots). Interestingly, they also found that patients who had poor oral hygiene but complied with the daily rinsing program had a significant reduction (from 91% to 50%) in white spot formation as well. The use of 1100-ppm fluoride toothpaste together with either a once-daily 0.05% NaF rinse (O'Reilly and Featherstone, 1987; Boyd, 1993) or twice-daily 0.4% SnF_2 gel (Boyd, 1993) is significantly more effective than the use of fluoridated toothpaste alone in preventing decalcification in adolescents undergoing treatment with fixed orthodontic appliances. This emphasizes the difficulty in attaining adequate plaque removal with fixed appliances, even with comprehensive initial toothbrushing instructions, the use of fluoridated toothpaste and monthly follow-up instructions and reinforcement. Daily 0.4% SnF_2 applications for 18 to 24 months also reduce white spot formation (Stratemann and Shannon, 1974).

However, compliance with rinsing protocols is an important issue. Geiger *et al.* (1992) reported poor compliance with fluoride rinsing regimens, assessed by using bottles with 10 mL dosimeters and recording the number of bottles used by each patient. The compliance results ranged from only 13% of children rinsing daily, to 42% rinsing every other day, and 45% of patients rinsing less frequently (Geiger *et al.*, 1992). Stratemann and Shannon (1974) also found poor compliance - only 52% of patients complied fully with daily SnF_2 gel application and 29% applied the gel once weekly or less. While higher compliance has been obtained with continued monthly reinforcement (Boyd, 1993), other authors found that poor compliance occurred even with special educational efforts and providing free fluoride rinse (Geiger *et al.*, 1992). Geiger *et al.* (1992) found that in compliant patients (those whose rinsed at least every other day) the occurrence of teeth with white spot lesion was 21% compared with 49% for less compliant children. The authors concluded that use of a 10 ml neutral sodium fluoride rinse at least every second day resulted in a significant reduction in white spot lesions, but methods to improve motivation and compliance must be found.

2.2.4 Chlorhexidine Treatments and Prevention of White Spot Formation

Lundström and Krasse (1987a,b) investigated the effectiveness of chlorhexidine treatments on the caries incidence in orthodontic patients with high levels of *Streptococcus mutans*. The experimental patients were treated with 1% chlorhexidine gel in custom trays at the beginning of treatment and whenever *S. mutans* levels exceeded $5x10^5$ CFU per ml of saliva (in addition to use of fluoridated toothpaste, and biweekly fluoride mouth rinses and/or annual topical fluoride application). They found no significant difference in caries incidence between the experimental patients and the control patients who received no chlorhexidine treatments, suggesting that other methods of preventing dental caries in orthodontic patients must be investigated.

2.2.5 Local Sustained-Release Materials

Given the important effects of fluoride on enamel and oral bacteria, along with the poor results achieved with mouthrinsing programs, it is obvious that a better solution needs to be found. Rawls (1991) summarized the potential advantages of sustained-release materials that can be placed in the mouth:

- The agent can be delivered directly to or near the disease site
- The systemic dosage can be minimized while the local therapeutic level is optimized
- The agent can be present continuously over an extended period
- The dosage can be maintained at a uniform level within the therapeutic range
- Direct involvement of health professionals is minimized
- The need for patient compliance is eliminated or reduced

It is important to determine whether any of the current orthodontic bonding materials fulfill some or all of these goals, and how they can be made more effective.

2.3 Bonding Materials Releasing Fluoride

2.3.1 Biomaterials and Nomenclature

With the advent of hybrid bonding materials ranging from composite resin to glass-ionomer, there has been much confusion over nomenclature (McLean *et al.*, 1994). As a result, McLean *et al.* (1994) recommended the following definitions:

- **Glass-ionomer cement:** cement that consists of a basic glass and an acidic polymer that sets by an acid-base reaction between these components.
- **Resin-modified glass-ionomer:** a material that sets partly by an acid-base reaction and partly by a photochemical polymerization. These materials retain a significant acid-base reaction as part of their overall curing process.
- **Polyacid-modified composite resin (a.k.a. compomers):** materials that contain either or both of the essential components of a glass-ionomer cement but at levels insufficient to result in the acid-base cure reaction in the dark.

2.3.2 Mechanisms of Setting and Fluoride Release

2.3.2.1 General Release Mechanisms

Rawls (1991) summarized the two general methods of releasing therapeutic agents from dental biomaterials:

- Materials with a release rate that gradually decreases with time:

    - Non-degradable – water from the oral environment diffuses into the matrix, dissolves the entrapped agent, which diffuses out in the direction of decreasing concentration. As time progresses, the agent must be leached from deeper within the matrix, causing the rate of release to fall
    - Degradable – occurs by dissolution or some other method of matrix erosion. Water diffuses in, degrades the matrix and releases the agent, causing the outer layers to be removed, reducing the surface area of the material (unless the eroding surface is flat, then the surface area remains the same and the rate of release does not change with time).
- Materials with a steady, linear release rate independent of time:
    - High loading/Matrix with low rate of diffusion – the required life of the delivery system must be less than the time needed to deplete enough agent to slow the rate of release.
    - Reservoir/Rate-controlling membrane barrier – a membrane slows the rate of diffusion from a solid solution or matrix in which the agent concentration is above the saturation limit.

2.3.2.2 Glass-Ionomer Cement

Extensive testing has shown that the fluoride release ability of conventional glass-ionomer is directly affected by the polycarboxylic acid-fluoroaluminosilicate glass setting reaction (Erickson and Glasspoole, 1995). Setting of this cement involves neutralization of the polyacid by the basic glass, with the formation of metal polyacrylate units

(Nicholson, 1998). The surface layer of the glass particle reacts with acid, while the glass core remains intact and acts as filler in the cement matrix. The surface layer of the glass powder becomes silicon-rich, and a silica gel layer is formed at the interface between the cement matrix and the glass particles (Saito *et al.*, 1999). During this acid-base reaction, fluoride along with many other ionic constituents is released. It has been hypothesized that the kinetics of fluoride elution from GIC involves two reactions (Tay and Braden, 1988). After reviewing the literature, Verbeeck *et al.* (1993) theorized that the first reaction involves a short-term surface process that reaches equilibrium, while the second process is a prolonged bulk diffusion that is responsible for long-term release of fluoride. Verbeeck *et al.* (1998) determined that it takes two weeks for this process to release 90% of the total amount of fluoride (measured in mg/cm^2, thus depending on the size of the specimen).

After reviewing the literature and analyzing their results, Verbeeck *et al.* (1998) suggest that once the glass-ionomer has set, the fluoride released by the set cement may originate from:

1. The remaining and not yet attacked leachable fluoride glass
2. The silica gel phase resulting from the acid-base reaction and covering the glass particles
3. The polysalt matrix where fluoride ions can be bound in strong complexes with the metal ions, especially aluminum
4. The pore liquid in which the fluoride ions are only loosely bound and free to move

The contribution of the first two sources was determined by leaching unreacted glass particles in water followed by acetic acid, and vice versa. It was shown that significant fluoride is released into the matrix when the acid attacks the glass during the setting reaction. However, when the glass particles come into contact with water, the fluoride release rate decreases rapidly and substantially to low levels (Verbeeck *et al.*, 1998). The authors stated that this might indicate that the silica gel layer is not a reservoir for the fluoride, but a barrier to further fluoride release from the remaining glass. The third and fourth sources relate to the organic matrix of the material and may also contribute to fluoride release. Glass-ionomer cement is cation permselective and fluoride transport across glass-ionomer cements is not based on simple diffusion. More specifically, the fluoride release depends on the time from start of the acid-base reaction to first contact of the set cement with an aqueous solution, with greater fluoride release when set cement is submerged in water 15 minutes after the start of mixing as compared with 1 day or 1 week (Verbeeck *et al.*, 1998). This effect of maturation is most probably the result of a change in the constitution of the matrix due to a loss of relatively soluble forms of fluoride during the cement's hardening and maturation.

2.3.2.3 Resin-Modified Glass-Ionomer Cement

As previously mentioned, resin-modified glass-ionomer cements set partly via an acid-base reaction and partly via a photochemical polymerization. These materials retain a significant acid-base reaction as part of their overall curing process (McLean *et al.*, 1994). However, Kakaboura *et al.* (1996) used MIR-FTIR (multiple internal reflection

Fourier transform infrared) spectroscopy to show that the acid-base reaction of resin-modified glass-ionomers is significantly slowed after light exposure. Momoi and McCabe (1993) postulated that for light-activated glass ionomer cements, the type and amount of resin used for the photochemical polymerization reaction might affect the rate of fluoride release. Once set, these hybrid materials have various mechanisms of releasing fluoride. The fluoride release can be due primarily to ion exchange, leaving the material intact (McCabe, 1998). Other materials show 'wash-out' or dissolution, which is characterized by leaching of ions other than fluoride, particularly calcium, leading to gradual disintegration of the material (Tam *et al.*, 1991; McCabe, 1998). In comparison with traditional glass-ionomer cements, fluoride release from Vitremer is significantly higher immediately after light cure than after 1 day, indicating that resin-modified glass-ionomers are moisture sensitive like their glass ionomer cement counterparts, but to a lesser extent (Verbeeck *et al.*, 1998).

2.3.2.4 Polyacid-Modified Composite Resin

Materials in this category are water-free, single-component, light-cured composites consisting of polyacid-modified dimethacrylate monomers reinforced with strontium or barium aluminosilicate glass particles (Eliades *et al.*, 1998). The setting reaction of a polyacid-modified composite resin is initiated by photo-polymerization, with the acidic monomer components polymerized to the acidic polymer, or the polymer with the acidic group (Saito *et al.*, 1999). The acid-base reaction is inhibited until the material hardens and absorbs water from saliva, when the acid group in the polymer reacts with the basic glass filler to produce a glass-ionomer core analog (Eliades *et al.*, 1998). Using FTIR spectroscopy, Eliades *et al.* (1998) stated that polyacid-modified composite surfaces stored in distilled water undergo a slow, solid-state transformation causing an acid-base reaction to produce carboxylate salts, reaching a saturation point after approximately 4 weeks. The glass particles in Dyract® were shown to degrade easily in pure water resulting in a significant release of fluoride, but the release rate decreased with time due to the development of a silica gel layer covering the glass particles (Verbeeck *et al.*, 1998). Polyacid-modified composite resins release considerably less fluoride than acid-base setting materials, but do not show moisture sensitivity since there is no difference in fluoride release immediately after curing or 24 hours later (Verbeeck *et al.*, 1998).

2.3.3 Fluoride Release Studies

Any potential benefit of fluoride-containing orthodontic bonding materials is dependent on the actualization of fluoride release from these materials. Studies have been conducted both *in vitro* and *in vivo* to determine fluoride release levels and duration from a variety of materials. Since the dental materials literature also contains substantial information on the fluoride release characteristics of restorative materials, these will be included along with orthodontic materials studied *in vitro* and *in vivo.*

2.3.3.1 Restorative Materials

It is well known that glass-ionomer cements release fluoride *in vitro* (Forsten, 1977). Creanor *et al.* (1994) found that discs (6 mm in diameter and 1.5 mm thick) of Vitrebond

(GIC) released a concentration of 155.2 ppm fluoride in 2 mL of deionized water at 24 hours, decreasing to only 3.99 ppm through to day 60. Forsten (1977) also found high release during the first 2 weeks, decreasing to low, but consistent levels by 2 months from samples with dimensions 2 mm x 2 mm x 12 mm (Forsten, 1977). This pattern has been termed a "burst effect", where the largest release of fluoride occurs in the first few days, and then tapers off to a lower, constant level (Ashcraft *et al.*, 1997). It has been shown that this low-level fluoride release is maintained long term. Wilson *et al.* (1985) reported that fluoride was still being released from samples of Chembond (GIC) after 598 days, Forsten (1990) found a fluoride concentration of at least 0.5 ppm in 5 mL of deionized water after 1 year in running non-fluoridated tap water (0.5 L/min) from samples 2.8 mm thick and 10.7 mm in diameter; and Forsten (1998) reported long-term fluoride release from GICs at such a constant level for a period exceeding 8 years.

Regarding the more recent resin-modified glass-ionomer materials, Momoi and McCabe (1993) found no significant difference in fluoride release between light-activated and conventional glass ionomer cements. Forsten (1998) also reported that 'true' resin-modified glass-ionomers released fluoride to the same extent and in a similar way to conventional GICs. This contrasted with the results of Creanor *et al.* (1994) who found that light-cured Fuji II LC released significantly less fluoride than Vitrebond GIC (at day 20 the concentration of fluoride released by Vitrebond was 1.47 ppm F^- while Fuji II LC had a concentration of 0.77 ppm F^- in 2 mL of deionized water).

Creanor *et al.* (1994) also found that the fluoride release pattern of the polyacid-modified composites Compoglass and Dyract was similar to those of glass-ionomer and resin-modified glass-ionomer materials in that there was high release initially followed by a low release period. However, the values were lower than those reported by Momoi and McCabe (1993) for resin-modified or traditional glass-ionomers (Eliades *et al.*, 1998). Forsten (1998) found evidence to the contrary, reporting that polyacid-modified composites (Variglass® and Dyract®) did not show a burst effect.

2.3.3.2 Orthodontic Bonding Materials

Cooley *et al.* (1989) determined fluoride release from Precise Paste and Paste Orthodontics Bonding System (resin) and Precise Glass Ionomer Band Cement (glass ionomer), as well as from Ketac-Fil (restorative glass ionomer). Precise Glass Ionomer released fluoride at a high rate on day 1 (112 $\mu g/cm^2$) but this diminished to 22 $\mu g/cm^2$ by day 7 and continued at 20 $\mu g/cm^2$ at three months. Ketac-Fil®, for comparison, released 200 $\mu g/cm^2$ on day 1, decreasing to 15 $\mu g/cm^2$ by day 7 and continuing at 17 $\mu g/cm^2$ at 3 months. Meanwhile, Precise Orthodontic Bonding Resin released 1 $\mu g/cm^2$ on day 1, dropping to 0.2 $\mu g/cm^2$ by day 3, and to undetectable levels from day 4 onward, indicating that it is ineffective for prolonged fluoride release.

Fox (1990) compared the release rate (in µg/day) of fluoride from a conventional GIC (Ketac-Cem®) with those from two no-mix composite orthodontic bonding materials (Direct® and Right-On®). Ketac-Cem® released the most fluoride, averaging 88 ± 6.3

over the first 2 days, falling to <0.1 by 10 weeks. Direct® (which claimed fluoride release) averaged 9.9 ± 1.1 for the first 2 days, falling to 0.24 ± 0.01 at 20 weeks. Right-On® (which did not claim fluoride release) released 2.9 ± 0.32 for the first 2 days, but by the second week it was down to 0.1 ± 0.01. The cumulative release patterns were also different; Ketac-Cem® had exponentially decreasing fluoride release rates over time, while Direct® and Right-On® had linearly decreasing release curves.

Wiltshire and Janse van Rensburg (1995) evaluated fluoride release from FluorEver OBA and Light-Bond. FluorEver OBA released approximately 35 μg F^-/cm^2 on the first day, dropping to 0.86 μg F^-/cm^2 by the third week. Fluoride release continued from week 17 through week 85 at levels ranging from 0.35 to 0.5 μg F^-/cm^2. Meanwhile, Light-Bond released approximately 5 μg F^-/cm^2 on the first day, falling to 0.11 μg F^-/cm^2 by the third week. Light-Bond failed to demonstrate long-term fluoride release, falling below the detection limit of the fluoride electrode by day 29.

In order to simulate more closely the clinical situation, Chan *et al.* (1990) used a tooth-bracket model to study fluoride release from a fluoride-releasing resin composite orthodontic adhesive (FluorEver OBA). They found that fluoride release was evident, and ranged from 52.6 ± 13.2 μg/cm^2 on day 3 to 10.5 ± 2.6 μg/cm^2 on day 43. They compared these results with fluoride release from larger discs of the same material, and reported that, as expected, fluoride release was much greater, but the pattern was similar to that with the tooth-bracket model.

Wiltshire (1999) studied release of fluoride from orthodontic elastomeric ligature ties. The 24-hour residual leachable fluoride in ligatures tested after one month of intraoral use was significantly greater than for those stored in distilled water. Fluoride-impregnated ligatures stored *in vitro* had mean 24-hour release of 0.02 μg F^- /mL/elastomeric ligature while those used in the mouth had 1.43 ± 0.37 μg F^- /mL/elastomeric ligature. Non-fluoridated ligatures also had higher fluoride content after 1 month of intraoral use when compared with *in vitro* storage. The non-fluoridated elastomerics released 0.44 ± 0.05 μg F^-/mL/elastomeric ligature after 1 month of intraoral use, while the controls samples released 0.003 μg F^-/mL/elastomeric ligature. The author concluded that residual, leachable fluoride is present in used elastomeric ligatures and that elastomeric ligatures imbibe fluoride *in vivo*.

2.3.4 Sample Size and Fluoride Release

As *in vitro* research attempts to investigate the properties of fluoride-releasing materials, the most appropriate sample shape for such tests is controversial. As mentioned previously, Cranfield *et al.* (1982) were interested in learning whether fluoride ions were derived from near-surface regions of the cement or from throughout the sample. They fabricated the cements into tubes of various lengths (1, 3, 5 and 10 mm) with only the end faces exposed to solution. Their data showed that fluoride release was greater with larger samples, regardless of similar surface area exposure. Williams *et al.* (1999) found evidence to the contrary using samples of conventional glass-ionomer in various shapes (cylinder, bar, disc) and sizes. Fluoride release from GIC (for up to 3 years) was dependent on sample surface area rather than volume. They also mentioned that had fewer cylinder sizes been used, a correlation between sample volume and fluoride release would have been found.

Wilson *et al.* (1985) found that discs that had a greater surface area (20 mm diameter x 1.5 mm thick) released proportionately greater amounts of fluoride than did cylinders (12 mm high x 6 mm diameter). Monteith *et al.* (1999) did not find such proportionality of fluoride release using three different models. They fabricated two sets of discs 3.0 mm in diameter x 1.5 mm thick of Vitremer (RMGIC), Dyract Ortho (polyacid-modified composite) and a composite resin control. They also bonded teeth in a tooth-bracket model using the same materials. One set of discs was coated with varnish on the upper and lower surfaces, halving the surface area. Their results showed that unvarnished discs with twice the surface area only released 1.2 to 1.5 times more fluoride than the varnished discs. Also, unvarnished discs released 3.0 to 4.5 times more fluoride than the tooth-bracket model, while varnished discs only released 2.2 to 3.7 times more fluoride (Monteith *et al.*, 1999). Thus it appears that the *in vitro* model used is important when considering the fluoride release levels, and choosing a tooth-bracket model would most closely simulate the *in vivo* situation.

2.3.5 Fluoride Re-release

It is important to have constant release of fluoride from fluoride-releasing materials, and it is therefore desirable to use a material that can be "recharged" with fluoride (Forsten, 1990). Since teeth are exposed to fluoride on a daily basis in the form of fluoridated toothpaste, mouthrinses, etc., as well as on a periodic basis to more concentrated fluoride (such as topical gels), it is essential to determine whether fluoride-containing orthodontic bonding materials are capable of imbibing fluoride from the environment.

Hatibovic-Kofman and Koch (1991) studied fluoride uptake and re-release from three glass-ionomer cements (Vitrebond®, Ketac-Fil® and ChemFil II®). After 11 weeks in distilled water the samples were exposed to toothpaste (250 ppm F^-) for 15 minutes. From the 11th to 12th weeks, the fluoride release of all materials increased. The concentration of fluoride released from Vitrebond® increased from 1.1 ± 0.9 ppm F^- to 31.3 ± 3.3 ppm F^-, Ketac-Fil® increased from 0.8 ± 0.8 to 15.3 ± 1.0 ppm F^- and ChemFil II® increased from 0.2 ± 0.9 to 11.2 ± 1.1 ppm F^-. Fluoride release subsequently decreased for each material up to the 16th week. The authors concluded that regular use of fluoridated toothpaste could result in the absorption of fluoride into glass-ionomer cements, and the subsequent fluoride release would increase fluoride levels in the oral environment (Hatibovic-Kofman and Koch, 1991).

Takahashi *et al.* (1993) investigated the use of different concentrations of fluoride for re-exposure. They exposed samples of various glass-ionomer cements and a fluoride-containing composite to 0.02%, 0.2% and 2% NaF solutions. They found that the amount of fluoride released after exposure was dependent on the concentration of the fluoride solution, and that the net amount of fluoride release was significantly higher after exposure to 2% NaF solution than to 0.02% or 0.2% NaF. Most glass-ionomers eluted fluoride at levels above control samples for a longer period following exposure to 0.2%

and 2% NaF, leading the authors to conclude that some fluoride must have diffused into the matrix of the material, thus acting as a reservoir for subsequent release. Interestingly, the fluoride-containing composite tested (Heliomolar Ro) released minimal fluoride and did not seem to bind fluoride after exposure (Takahashi *et al.*, 1993).

Creanor *et al.* (1994) reported fluoride re-release from various glass-ionomer cements. The samples were stored in 1 L of water each for 60 days to leach most of the fluoride. They were then exposed to 1000 ppm F^- daily for 20 days and compared with unexposed control samples. While the control samples released small concentrations, the test samples consistently released more fluoride (Creanor *et al.*, 1994).

Ashcraft *et al.* (1997) tested three light-cured glass-ionomers (Band-Lok, Zionomer and Geristore) using a tooth-bracket model. On day 48 (after bonding) the samples were exposed to 0.4% SnF_2 gel for 30 seconds. The concentration of fluoride released from Band-Lok cement increased to 78% (1.50 ppm on day 1; 1.17 ppm on day 49) of initial levels after exposure to fluoride, while Zionomer increased to 70% (0.36 ppm on day 1; 0.25 ppm on day 49) and Geristore to 63% (0.50 ppm on day 1; 0.32 ppm on day 49). The concentration of fluoride released by the composite resin control (Concise) increased 300% the day after fluoride gel exposure than on the first day after bonding (0.04 ppm on day 1; 0.12 ppm on day 49). The fluoride released from teeth bonded with composite resin showed that the exposed enamel, bracket surface and composite resin could adsorb and release small amounts of fluoride (Ashcraft *et al.*, 1997).

2.3.6 Cariostatic Effect of Fluoride-Releasing Orthodontic Bonding Materials

It is essential to realize that fluoride release from orthodontic bonding materials is of importance only if cariostatic effects are imparted to the bonded teeth. The ultimate goal of using fluoride-releasing materials, as a supplement to good oral hygiene, is to decrease or prevent the incidence of white-spot decalcification. Only if such benefits can be demonstrated will the use of such materials be of value.

2.3.6.1 *In vitro* studies

The caries inhibitory effect of fluoride-releasing adhesives used for orthodontic bonding has been demonstrated in several studies (Valk and Davidson, 1987; Kindelin, 1996; Basdra *et al.*, 1996; Vorhies *et al.*, 1998). Valk and Davidson (1987) bonded brackets to bovine enamel and showed that, after demineralization treatment, glass-ionomer protected a substantial area of uncovered enamel adjacent to the cemented bracket. This was in contrast to traditional composite resin, which showed caries even underneath the bonded bracket. Kindelan (1996) showed that the fluoride-releasing bonding agents Ketac-Cem® (GIC) and Pulpdent OBA® (polyacid-modified composite) protected extracted human premolars from demineralization, while Rely-a-Bond® (polyacid-modified composite) did not afford such protection. Basdra *et al.* (1996) contradicted this result by reporting that Rely-a-Bond and Fluorobond/Concise (fluoride-releasing sealant and traditional composite resin) showed significantly less enamel demineralization in an acidic medium. This correlated with fluoride-release data, showing that Fluorobond/Concise released the most fluoride and offered the best protection from demineralization. Vorhies *et al.* (1998) used polarized light microscopy to show that teeth bonded with hybrid glass ionomer cements (Advance® and Fuji Ortho™ LC) provided significant protection from demineralization compared with a composite resin control (Transbond XT®). Interestingly, brushing twice daily with fluoridated toothpaste (1500 ppm F^-) reduced enamel lesion depths for the Transbond XT group, but not for the fluoride-releasing groups. This led the authors to attribute most of the inhibition of enamel demineralization to fluoride release from the materials, with a small contribution from topical fluoride in the toothpaste.

2.3.6.2 *In vivo* studies

Successful inhibition of enamel demineralization *in vitro* by fluoride-releasing orthodontic bonding materials has also been demonstrated *in vivo* (Sonis and Snell, 1989; Øgaard *et al.*, 1992; Underwood *et al.*, 1989; Chung *et al.*, 1998). In following orthodontic patients through the full course of treatment, Sonis and Snell (1989) bonded opposite quadrants with either Fluorever (fluoride-releasing composite) or Aurafill (traditional composite). They found that teeth bonded with FluorEver showed no decalcification, as compared with control teeth that had a 12.6% overall decalcification rate. Øgaard *et al.* (1992) used microradiography to demonstrate that a fluoride-containing adhesive (Orthodontic Cement VP 862) reduced lesion depths by 48% during a 4-week *in vivo* period when compared with samples bonded with Heliosit Orthodontic (fluoride-free composite resin). Underwood *et al.* (1989) bonded teeth *in vivo* with either Concise (control) or an experimental fluoride-exchanging resin and extracted those teeth after 60 days. To determine enamel lesion depth they used a polarized light microscopy method with either water or quinoline (to show dark zone formation). With water imbibition, 5 to 25% pore volume (showing the body of the lesion) was found in 2.78% of teeth bonded with fluoride-exchanging resin and 1.73% with Concise. However, with quinoline as the imbibition medium, dark zone formation (which is a more reliable indicator of early demineralization) indicated by 2 to 4% pore volume, was found in 2.3% of teeth bonded with fluoride-exchanging resin and 33.5% for Concise, a 93% reduction in the early enamel demineralization stages (Underwood *et al.*, 1989). Chung *et al.* (1998) compared extracted teeth one month after bonding with Vitremer® (resin-modified glass-ionomer), Dyract® Ortho (polyacid-modified composite) and Right-On (control composite). They found that the Vitremer® and Dyract® Ortho group combined had significant reduction in enamel demineralization, but each group individually showed no significant differences from the control group.

Some studies have not shown the enamel protection benefits of fluoride-releasing materials (Mitchell, 1992; Banks *et al.*, 1997; Millett *et al.*, 1999). Mitchell (1992), using a photographic technique, found that Direct® did not result in significant protection against enamel decalcification during orthodontic treatment. Banks *et al.* (1997) supported *in vitro* data (Kindelan, 1996) by reporting that Rely-a-Bond did not significantly reduce enamel decalcification *in vivo*. Millett *et al.* (1999) compared Ketac-

Cem (GIC) and Right-On (composite resin control) using a split-mouth design for an extended treatment time (averaging 15.3 months), and found no significant difference in the incidence of enamel decalcification between the groups.

Fluoride release studies of orthodontic bonding materials are only relevant if the level of fluoride release required to provide protection from enamel demineralization can be determined. For this to occur, it is necessary to correlate *in vitro* and *in vivo* data. Rawls (1995) reviewed the literature on fluoride-releasing resin-based dental materials in an attempt to determine the lowest effective level of fluoride required for caries protection. He states "to inhibit caries initiation in sound enamel in the vicinity of a resin-based dental material...exposed to the oral environment: 0.65 to 1.3 $\mu g\ F^-/cm^2/d$ for specimens exposed on one side and having thickness of up to about 2 mm" is necessary. In summary, there is a potential benefit for fluoride-releasing bonding materials in orthodontics, provided adequate fluoride release rates are achieved.

Chapter 3

Methods and Materials

3.1 Materials used in this study

3.1.1 Fuji Ortho™ LC

Fuji Ortho™ LC is a light-cured resin-modified glass ionomer in powder-liquid form and requires mixing (Lai *et al.*, 1999). The powder is composed of fluoroaluminosilicate glass and the liquid contains hydroxyethyl methacrylate (HEMA), water copolymer of acrylic and maleic acids, and activator. The liquid also contains camphorquinone as a photoinitiator (Lai *et al.*, 1999).

Material	Manufacturer	Lot Number
Fuji Ortho™ LC	(GC America Inc., Alsip, IL)	071267

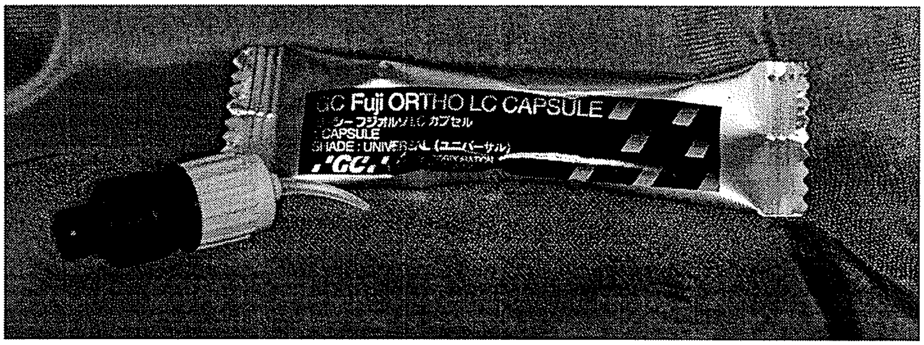


Figure 5: Fuji Ortho™ LC

3.1.2 Python™

Python™ is a light-cure, no-mix bonding system. It is a bisphenol A diglycidylmethacrylate (Bis-GMA) system containing a pre-polymerized acrylic modified resin with an acrylic monomer and containing glass particles as an active filler (McNeill, 2000). Python™ contains >20% Bis-GMA, >1% polyethyleneglycol dimethacrylate, >0.5% benzoyl peroxide, 5-10% aluminum oxide, and 10-35% fumed silica (M.S.D.S. 151-100, 151-105).

Material	Manufacturer	Lot Number
Python™	TP Orthodontics, LaPorte, IN, USA	CE 0646 (no fault)

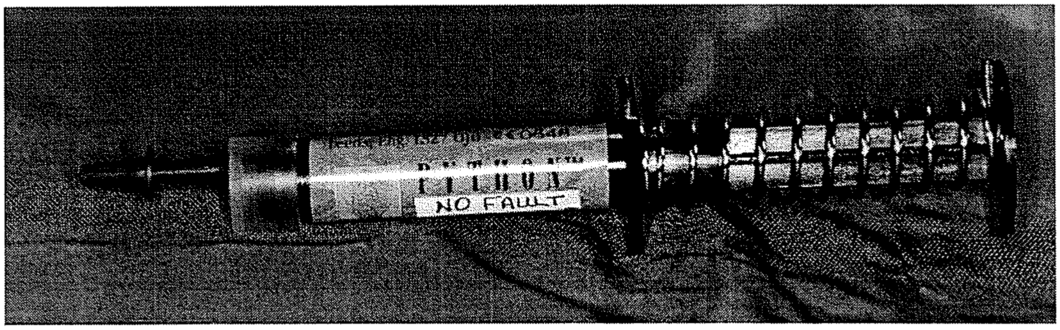


Figure 6: Python™

3.1.3 Assure™

Assure™ (Reliance Orthodontic Products Inc., Itasca, IL) is described by the manufacturer as a "fluoride-releasing light cure sealant paste system for wet or dry environment" (Assure™ product literature, 2001). Assure™ paste contains 8-30% hydroxyethyl methacrylate, 60-99% glass frit and 1-5% sodium fluoride (Assure™ M.S.D.S, 1998). The US-EPA description of *frit* "is a mixture of inorganic substances produced by rapidly quenching a molten, complex combination of materials confining the chemical substances thus manufactured as non-migratory components of glassy solid flakes or granules" (Assure™ M.S.D.S., 1998). Assure™ primer contains 15-40% biphenyl dimethacrylate and 40-70% acetone (Assure™ Primer M.S.D.S, 1998).

Material	Manufacturer	Lot Number
Assure™ Paste	Reliance Orthodontic Products Inc., Itasca, IL, USA	039188 (Part 1) 002240 (Part 2)
Assure™ Light Cure Sealant Resin/Primer	Reliance Orthodontic Products Inc., Itasca, IL, USA	002180

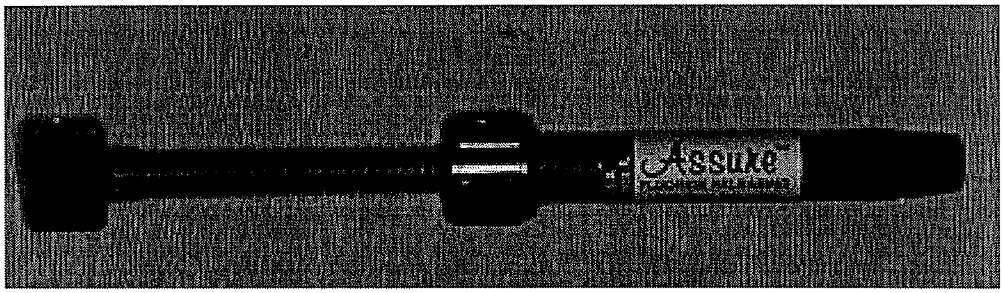


Figure 7: Assure™ Paste

Figure 8: Assure™ Primer and Etching Agent

3.1.4 Quick Cure™

Quick Cure™ (Reliance Orthodontic Products Inc., Itasca, IL) is described by the manufacturer as a "fluoride-releasing light cure bracket bonding system", and is a "new generation of light cure paste that provides a much broader area of sensitivity to blue light for a faster and more complete cure" (Quick Cure™ Product literature, 2001). Quick Cure™ contains unspecified percentages of fused silica, bisphenol A diglycidylmethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) (Quick Cure™ M.S.D.S., 2000).

Material	Manufacturer	Lot Number
Quick Cure™ Paste	Reliance Orthodontic Products Inc., Itasca, IL, USA	004100
Assure™ Sealant	Reliance Orthodontic Products Inc., Itasca, IL, USA	002180

Figure 9: Quick Cure™ Paste

3.1.5 Transbond™ XT

Transbond™ XT is a no-mix paste-liquid light-cured composite adhesive (Lai *et al.*, 1999). The paste is composed of approximately 18% Bis-GMA/TEGDMA monomers and approximately 82% hybrid filler (3 μm silica particles) with adiketone and organic amine as photoinitiators. The liquid primer is composed of Bis-GMA in combination with a urethane oligomer (Lai *et al.*, 1999).

Material	Manufacturer	Lot Number
Transbond XT™ light cured adhesive paste	3M Unitek™, Monrovia, CA, USA	062697 (Part 1) 0AK (Part 2)
Transbond XT™ primer	3M Unitek™, Monrovia, CA, USA	0AC
Dentsply 34% tooth conditioner gel	Dentsply Canada, Woodbridge, ON, Canada	9912021

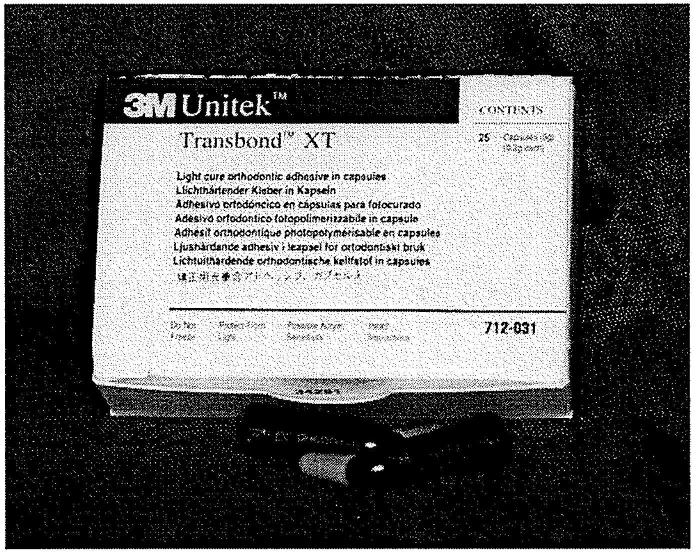


Figure 10: Transbond™ XT (Part I)

Figure 11: Transbond™ XT (Part II)

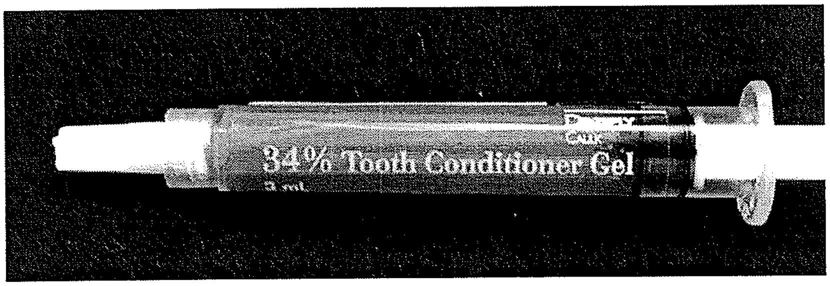


Figure 12: Dentsply 34% Tooth Conditioner Gel

3.1.6 Orthodontic brackets

Thirty pre-adjusted upper left first premolar edgewise orthodontic brackets (American Orthodontics, Sheboygan, WI) were used for bonding to teeth in part II of the study. Using a scientific digital image analysis software program (SigmaScan Pro®, SPSS Inc., Chicago, IL) the bracket base perimeter was calculated to be 1.185 cm.

Bracket	Manufacturer	Lot Number
Upper left first premolar brackets	American Orthodontics, Sheboygan, WI, USA	Unknown

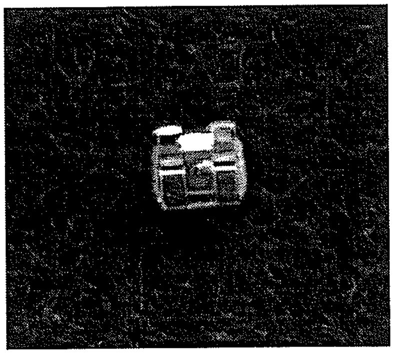


Figure 13: Upper left first premolar bracket

3.1.7 Teeth

Thirty-one intact, caries-free human premolar teeth extracted for orthodontic purposes were collected. These teeth were stored for at least two weeks in de-ionized, distilled water to allow free fluoride ions within the tooth to diffuse out (Monteith *et al.*, 1999). One tooth was used in a pilot study to determine whether the varnish used would prevent fluoride release from the tooth. The thirty remaining teeth were used in part II of the study.

3.1.8 Varnish

The varnish used to prevent fluoride release from the teeth was Color Fast!™, a clear, one coat, fast dry varnish (Sally Hansen, Del Laboratories (Canada) Inc., Barrie, ON). A pilot study was done to confirm that the varnish would not release fluoride. One tooth was completely coated with the varnish and placed in 5 mL of de-ionized distilled water for 7 days. The water was subsequently tested for fluoride and none was detected.

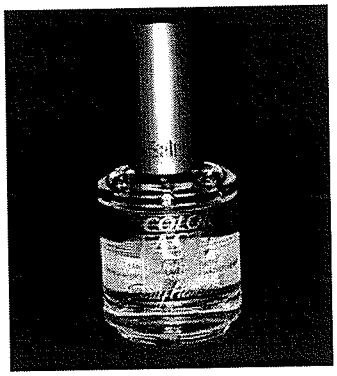


Figure 14: Color Fast!™ Varnish

3.2 Experimental Method – Part I

Part I of this study is the continuation of a previous research project (McNeill, 2000). The following sections reiterate the experimental methods used in that study:

3.2.1 Preparation of Specimens

In the previous study, specimens were fabricated using a steel and Teflon split-mould machined at the University of Pretoria, South Africa.

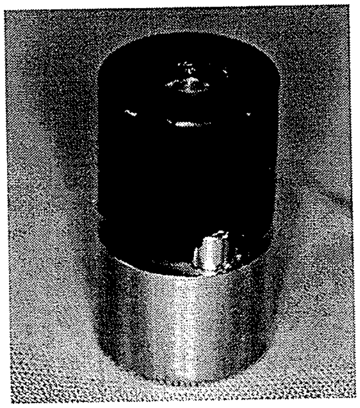


Figure 15: Split-mould

Twenty standard-sized specimens (6 mm in diameter and 2 mm in thickness) of each of the following materials were manufactured:

1. Transbond™ XT (3M Unitek™, Monrovia, CA)
2. Python™ (TP Orthodontics, LaPorte, IN)
3. Assure™ (Reliance Orthodontic Products Inc., Itasca, IL)
4. Fuji Ortho™ LC (GC America Inc., Alsip, IL)

3.2.1.1 Transbond™ XT

A capsule of Transbond™ XT adhesive paste was placed in the application gun supplied by the manufacturer and the paste was expressed into the mould, avoiding inclusion of voids. The Transbond primer was not used. The mould was filled flush to the top with adhesive paste. (from McNeill, 2000)

3.2.1.2 Python™

The syringe tip of Python™ adhesive paste was held just over the mould as the paste was expressed into the split-mould. The mould was filled completely. Neither Python™ conditioning liquid nor sealant was used. (from McNeill, 2000)

3.2.1.3 Assure™

Adhesive paste from the syringe was expressed into the split-mould in the same manner as described for Python™. The light-cure sealant was not used. (from McNeill, 2000)

3.2.1.4 Fuji Ortho™ LC

The adhesive-filled capsule was squeezed together by hand to break the membrane separating powder and liquid. The capsule was then triturated for 10 seconds in a Vari-Mix III triturator (Caulk/Dentsply, Milford, DE) at approximately 4000 oscillations/minute. The capsule was then loaded into the application gun supplied by the manufacturer and the adhesive paste was squeezed into the mould. (from McNeill, 2000)

3.2.1.5 Sample Manufacturing Technique

When the split-mould was filled flush to the top with a sample of each type of the uncured bonding material, a clear Mylar strip (Palmero Health Care, Stratford, CT), was held with light finger pressure over the unset material, in contact with the superior surface of the mould.

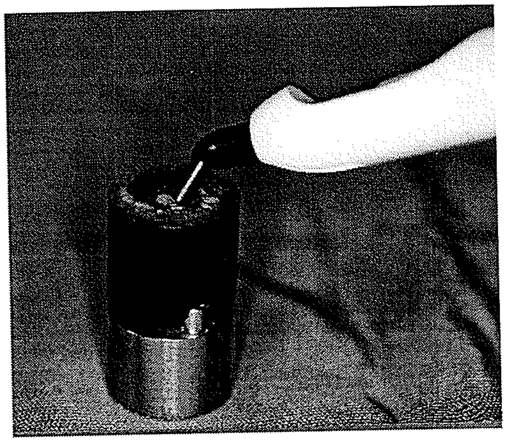


Figure 16: Filling the split-mould

An Ortholux™ XT Visible Light Curing Unit (3M Unitek™, Monrovia, CA) was used to light-cure all materials. The light tip was held directly over, but not in contact with, the sample. Curing time was 40 seconds per specimen for all material types.

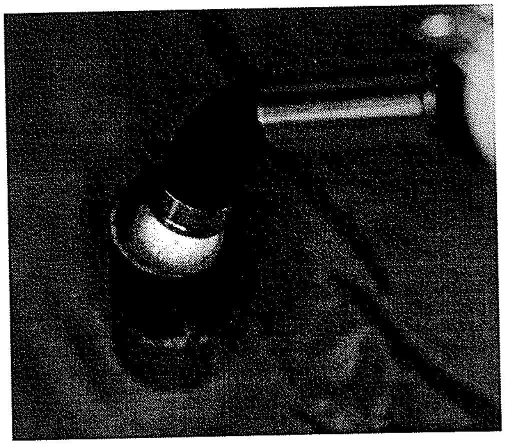


Figure 17: Light curing material in the split-mould

Once curing was completed, each specimen was released from the mould.

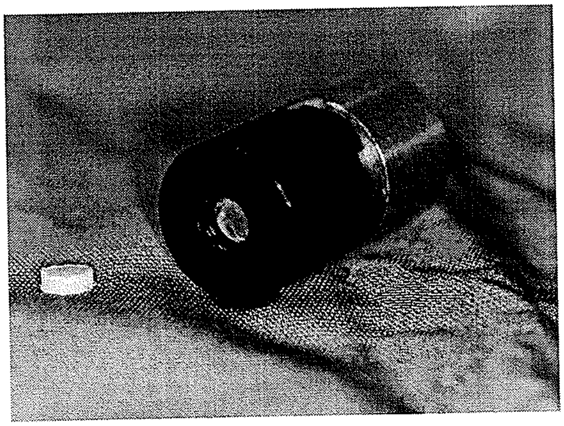


Figure 18: Sample released from split-mould

All discs were then weighed on a model 2001 MP2 electronic analytical balance (Sartorius, Gottingen, Germany) to the nearest 0.0001 g. Each disc was then placed into an individual 10 mL polyethylene test tube (#14-956-3D, 12x75 mm with snap caps, Fisher Scientific, Pittsburgh, PA), and labelled with the material type and specimen number.

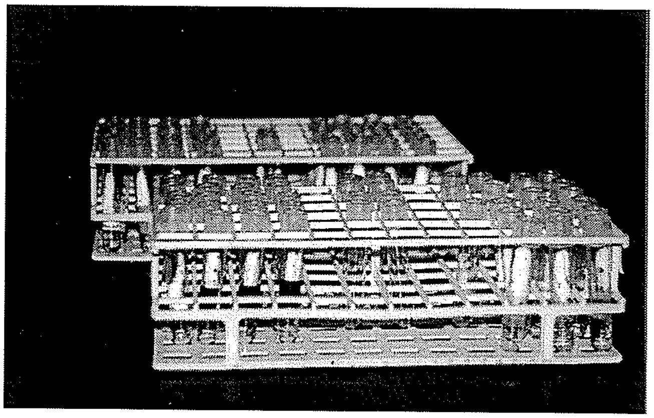


Figure 19: Samples in polyethylene test tubes

A time period of 24 hours elapsed between fabrication of the specimens and immersion in sample solutions, during which time the samples were maintained in their test tubes in an incubator (Thelco Precision Scientific, model #18, Chicago, IL) at 37°C and 100% relative humidity. The surface area of the discs was calculated using the formula $[\pi dh]+[2\pi(r^2)]$, as stated by Monteith *et al.* (1999). The calculated surface area of each specimen was 0.9425 cm^2. (from McNeill, 2000)

3.2.2 Specimen storage

De-ionized distilled water was used as the immersion solution for 10 samples of each material. Using an automatic pipette (Brinkman Dispensette 2 mL, Westbury, NY), 1 mL of water was added to 10 test tubes for each material, for a total of 40 specimens. The remaining 40 specimens were immersed in 1 mL of artificial saliva. However, McNeill (2000) found that at later time periods no differences in fluoride release were noted for the materials in distilled water vs. artificial saliva. As a result, it was decided only to follow the discs immersed in de-ionized distilled water for long-term study. All test tubes were capped with their polyethylene covers, placed in racks and stored in an incubator at 37°C and 100% relative humidity. This temperature was chosen since some glass-ionomers release more fluoride at 37°C than at 21°C (Jones *et al.*, 1987). To prevent measurements from being cumulative, solutions were changed 24 hours before the samples were analyzed (Cooley *et al.*, 1989). (from McNeill, 2000)

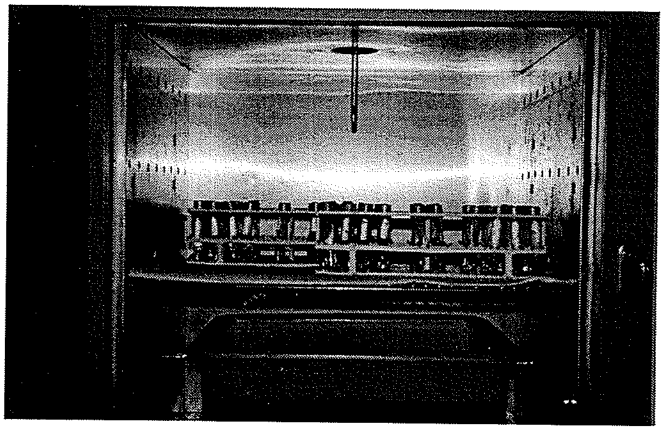


Figure 20: Samples stored in incubator

3.2.3 Measurement of Fluoride Release

3.2.3.1 Fluoride Electrode Calibration and Use

A fluoride ion-specific combination electrode (model 13-620-528, Orion Research Inc., Beverly, MA) connected to a pH meter (Radiometer pHM 82 standard pH meter, Copenhagen, Denmark) was used to measure fluoride in solution (Fox, 1990). When not in use, the electrode was immersed in a standard fluoride solution as per manufacturer instructions.

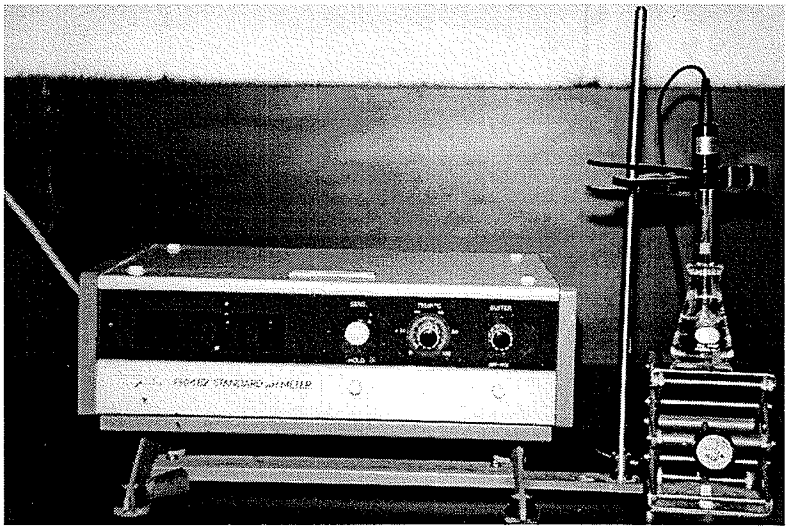


Figure 21: Fluoride electrode setup

The electrode was calibrated using a series of standard solutions made from the serial dilution of NaF in de-ionized, distilled water. The standard solutions were of the following concentrations (in ppm): 1000, 100, 10, 1, 0.6, 0.3 and 0.1. Using these standard solutions, a calibration curve of parts per million (ppm) vs. millivolts (mV) was plotted on semi-logarithmic graph paper (Fox, 1990). A new calibration curve was plotted at the beginning of each session. The ion-specific electrode operates on the principle that a potential develops across the electrode's membrane, and the relationship between this potential and fluoride ion activity is governed by the Nernst equation:

$$\mathbf{E = E^\circ - S \log A}$$

E = measured electrode potential

E° = constant, sum of several system potentials

S = electrode slope

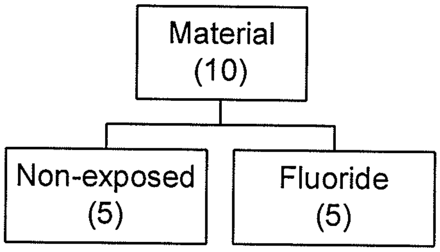
A = fluoride ion activity

The ideal Nernstian equation slope is –58 mV per decade increase in fluoride ion activity (at 20°C), except at very low fluoride concentrations (Rix, 1999; from McNeill, 2000).

For fluoride measurement, the 1 mL sample solution was transferred into a 5 mL polyethylene test cup (Nalgene, Rochester, NY). An equal amount (1 mL) of TISAB II (Orion Research Inc., Beverly, MA) was added to each sample, and then allowed to adjust to room temperature (from McNeill, 2000). Since the fluoride ion-selective electrode is sensitive to changes in pH, TISAB (Total Ionic Strength Adjustment Buffer) must be added to any water specimen to hold the pH of the specimen between 5.0 and 5.5. TISAB frees F^- ions bound to hydrogen, and eliminates hydroxyl ion interference, enabling accurate measurement of total fluoride content (Fox, 1990). The electrode was rinsed thoroughly with de-ionized, distilled water and placed in the sample solution. The electrode was allowed to stabilize before measurements were taken. The electrode was rinsed thoroughly with de-ionized, distilled water between each measurement. Using the calibration curve described previously, the concentration of each sample (ppm) was determined from the mV reading given on the pH meter. (from McNeill, 2000)

3.2.3.2 Fluoride Measurement Schedule

In the preceding part of the study, fluoride release measurements were taken for all samples at 6 hours, 24 hours, 3 days, 7 days, 14 days, 21 days, 1 month, 2 months, 3 months, 4 months, 5 months and 6 months. For the present study, each of the four sample groups (Fuji Ortho™ LC, Assure™, Python™ and Transbond™ XT) was divided in half, leaving eight groups of five samples each (see chart below).



The "non-exposed" group of each material had fluoride-release measurements taken at days: 546 (18 months), 637 (21 months), 730 (24 months), 821 (27 months) and 913 (30 months) from the time of initial fabrication. At day 545 (18 months) from time of initial sample fabrication, the "fluoride" group was re-exposed (submerged) in 2% NaF gel (Nupro, Dentsply Canada Ltd, Woodbridge, ON) for 4 minutes, rinsed, gently dried and replaced in de-ionized distilled water (Takahashi *et al.*, 1993), and had measurements taken at 24 hours (day 546 from initial fabrication), 3 days (day 548), 7 days (day 552), 1 month (day 575), 3 months (day 637), 6 months (day 730), 9 months (day 821) and 12 months (day 913) following fluoride exposure.

3.2.4 Statistical Analysis

The results of fluoride-release testing on days 546, 548, 552, 575, 637, 730, 821 and 913 for the fluoride exposed samples, and on days 546, 637, 730, 821 and 913 for the non-exposed samples, were each analyzed using a two-tailed repeated measures analysis of variance (ANOVA) at the 5% significance level to determine whether significant differences in fluoride-release rates existed between the different sample groups and within each group over time for both the fluoride-exposed and non-exposed samples (Hassard, 1991).

3.3 Experimental Method – Part II

3.3.1 Preparation of Specimens

Thirty tooth-bracket specimens were fabricated using human premolars extracted for orthodontic reasons. Each tooth was removed from the de-ionized distilled water storage medium and dried gently. The crown of each tooth was cleaned with fluoride-free pumice (Preppies™, Whip Mix Corporation, Louisville, KY) using a slow-speed prophylaxis cup.

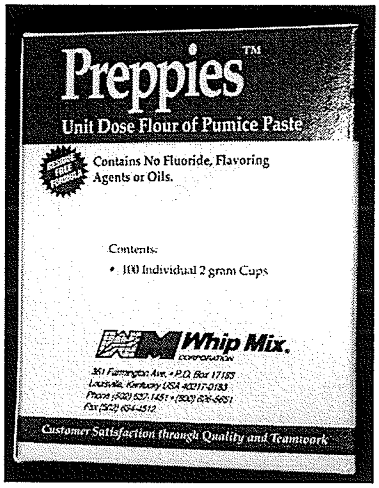


Figure 22: Preppies™ pumice paste

For the bonding procedure, a template was fabricated from paraffin wax to limit the bonding materials to the bracket base area. As such, a hole was cut in the paraffin wax to the dimension of the orthodontic bracket base, and was kept in place throughout the bonding procedure.

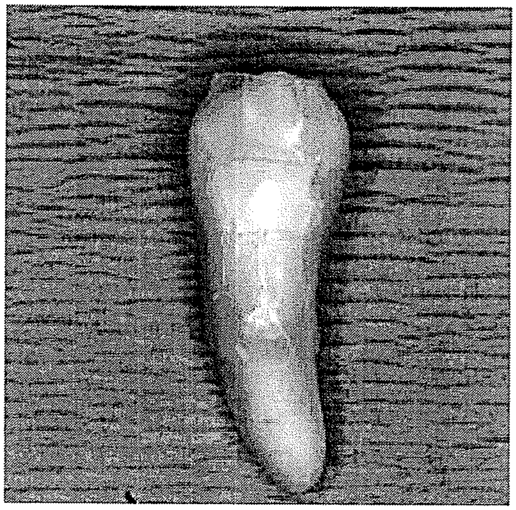


Figure 23: Buccal view of paraffin wax template on tooth

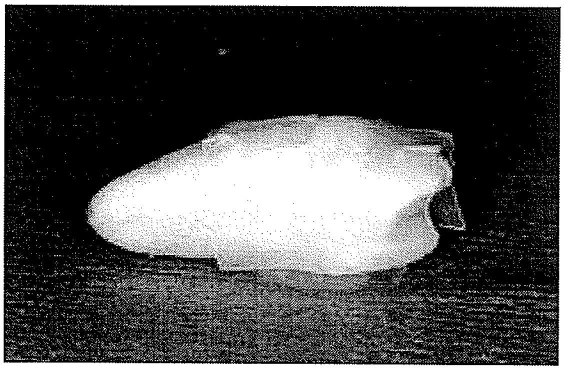


Figure 24: Lateral view of paraffin wax template on tooth

Ten teeth were bonded with pre-adjusted edgewise orthodontic brackets (American Orthodontics, Sheboygan, WI) for each of the bonding materials (Assure™, Quick Cure™ and Transbond™ XT) according to manufacturers' instructions. The template was placed on the tooth, which was then prepared with the appropriate etching and bonding materials. The bracket base was coated with bonding resin and placed on the tooth within the defined bonding area. To minimize further residual excess bonding material, a dental explorer was used to clean around the bracket base before curing the material (Monteith *et al.*, 1999).

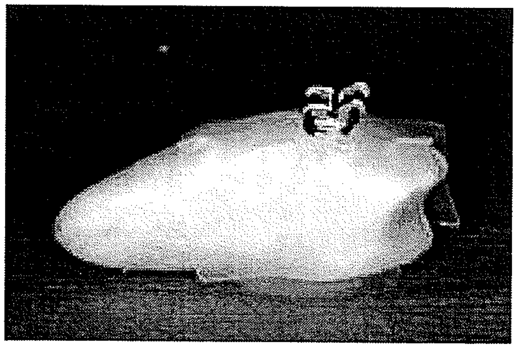


Figure 25: Bracket bonded with paraffin wax template in place

Each sample was then cured with an Ortholux™ Curing Light (3M Unitek™, Monrovia, CA). The surface area of exposed material around the bracket base periphery was calculated using the formula A = l x ht, where length was the perimeter of each bracket base and height was the thickness of material at the bracket periphery estimated at 0.01 cm (Rix, 2000). The calculated surface area for material exposed at the bracket base periphery was 0.01185 cm^2.

Figure 26: Ortholux™ Light-Curing Unit

After light curing, each tooth was coated with a layer of fluoride-free varnish to prevent leaching of fluoride from tooth material for the duration of the experiment. The varnish was applied with a brush to the tooth, coming as close as possible to the edge of the bracket without coating the bracket or bonding resin (Monteith *et al.*, 1999).

3.3.1.1 Assure™

10 teeth were randomly chosen for bonding with Assure™ (Reliance Orthodontic Products Inc., Itasca, IL) according to manufacturer's instructions. Reliance etching agent (37% phosphoric acid) was placed on the bonding area for 30 seconds. The etching agent was then rinsed thoroughly with water for 10 seconds and dried thoroughly so that a frosty white appearance was evident. Assure™ sealant was then applied to the prepared

area of each tooth. Assure™ paste was then applied and worked into the bracket base using a spatula, and the bracket was pressed into position on the tooth. Excess material was removed using a dental explorer, and the paste was cured with the Ortholux™ (3M Unitek™, Monrovia, CA) light-curing unit for 20 seconds from the incisal edge and 10 seconds from the gingival edge.

3.3.1.2 Quick Cure™

10 teeth were randomly chosen for bonding with Quick Cure™ (Reliance Orthodontic Products Inc., Itasca, IL) according to manufacturer's instructions. Reliance etching agent was placed on the tooth bonding area for 30 seconds. Using an air/water syringe the tooth was rinsed thoroughly for 10 seconds and dried until a frosty white appearance was seen. Assure™ sealant was generously applied to the tooth, allowed to sit for 10 seconds, lightly dried with air for 5 seconds and light cured for 10 seconds. Quick Cure™ paste was applied and worked into the bracket base and the bracket pressed into position on the tooth. Each bracket was cured with the Ortholux™ (3M Unitek™, Monrovia, CA) light-curing unit for 5 seconds from the incisal and 5 seconds from the gingival edges.

3.3.1.3 Transbond™ XT

10 teeth were randomly chosen for bonding with Transbond™ XT (3M Unitek™, Monrovia, CA) according to manufacturer's instructions. 34% phosphoric acid etch (Dentsply Canada, Woodbridge, ON) was placed on the tooth for 15 seconds, rinsed thoroughly with water and dried thoroughly. A thin coat of light cure adhesive primer

was applied to the etched area. Adhesive was applied to the bracket base and the bracket was seated on the tooth. The adhesive was then light cured with the Ortholux™ (3M Unitek™, Monrovia, CA) light-curing unit for 10 seconds from the incisal edge and 10 seconds from the gingival edge.

3.3.2 Specimen Storage

De-ionized distilled water was the storage medium used for storing the tooth-bracket samples (McNeill, 2000). Water was added to glass jars with an automatic pipette (Brinkman Dispensette 5 mL, Westbury, NY). The bonded teeth were placed into the water, ensuring that the bracket and crown of the tooth were submerged in the water. For days 1 and 3, 5 mL of water was placed in each jar. From day 7 on, 2.5 mL of water was used to allow more accurate fluoride measurement. The jars were placed in an incubator at 37°C and 100% relative humidity for reasons discussed in section 3.2.2. Again, to prevent cumulative measurement of fluoride, the storage solutions were changed 24 hours before measurement (Cooley *et al.*, 1989).

3.3.3 Measurement of Fluoride Release

3.3.3.1 Fluoride Electrode Calibration and Use

A new fluoride detection procedure was used for part II of this study, incorporating more modern fluoride detection equipment. Fluoride levels in de-ionized distilled water were measured with a fluoride ion-specific combination electrode (Orion model 96-09, Orion Research Inc., Beverly, MA) attached to a pH/ISE/ORP measurement system

(Sensorlink™ PCM700, Orion Research Inc., Beverly, MA) and a laptop computer (IBM Thinkpad I Series, IBM Corporation, Armonk, NY). When not in use, the electrode was stored as per manufacturer instructions. The electrode was calibrated at each measurement session with a series of standard solutions created from the serial dilution of 1000 ppm NaF. The standard solutions were of the following concentrations (in ppm): 1000, 100, 10, 1, 0.6, 0.3, 0.1. The Orion computer software calculated an appropriate calibration curve of parts per million (ppm) vs. millivolts (mV) based on the standard samples. For samples collected on days 1 and 3, the 5 mL samples were added to 0.5 mL TISAB III buffer, for reasons discussed in section 3.2.3.1. For samples collected at day 7, 1 month, 3 months and 6 months, 2.5 mL of de-ionized distilled water was combined with 0.25 mL of TISAB III. TISAB III is a concentrated version of the buffer, so the amount of buffer is only 1/10 the volume of the sampled being measured. The sample was allowed to reach room temperature before measurement.

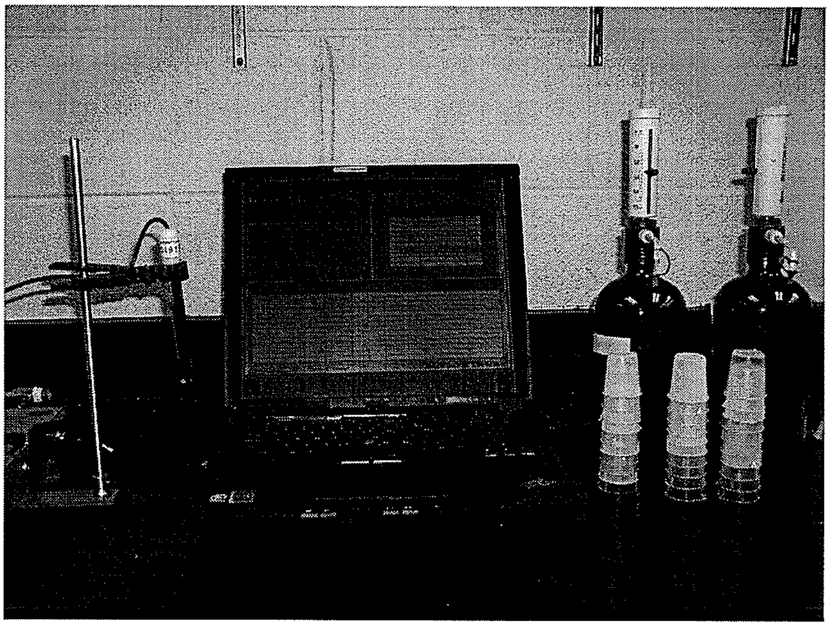


Figure 27: Fluoride measurement apparatus

3.3.3.2 Fluoride Measurement Schedule

After fabrication and immersion in deionized distilled water, fluoride-release measurements were taken on day 1 (24 hours), day 3, day 7, day 30 (1 month), day 90 (3 months) and day 180 (6 months). Storage water was changed 24 hours prior to testing to avoid cumulative measurement of fluoride release (Cooley *et al.*, 1989).

3.3.4 Statistical Analysis

The results of fluoride-release testing on days 1, 3, 7, 30, 90 and 180 were analyzed using a two-tailed repeated measures analysis of variance (ANOVA) at the 5% significance level to determine whether significant differences in fluoride-release rates existed among the different sample groups and within each group over time (Hassard, 1991).

Chapter 4

Results

4.1 Long-term Fluoride Release

4.1.1 Overall Pattern

Fuji Ortho™ LC always released the highest levels of fluoride, followed by Python™ and Assure™. The control material, Transbond™ XT, never released detectable levels of fluoride. The long-term fluoride release rates for all materials are found in Table 1. The fluoride release measurements for individual samples can be found in Appendix 1.

Table 1: Long-term fluoride release rates (mean ± S.E., n=5)

Material	Fluoride Release ($\mu g/cm^2/day$)				
	Day 546* (18 months)	Day 637 (21 months)	Day 730 (24 months)	Day 821 (27 months)	Day 913 (30 months)
Fuji Ortho™ LC	11.04 ± 0.27 a A	10.45 ± 0.040 a A	10.18 ± 0.071 a A	10.15 ± 0.052 a A	10.33 ± 0.031 a A
Python™	8.09 ± 0.21 b A	5.79 ± 0.43 b B C	4.47 ± 0.20 b B	6.19 ± 0.36 b C	6.77 ± 0.21 b A C
Assure™	7.68 ± 0.65 b A	4.62 ± 0.79 b B	1.04 ± 0.14 c C	1.21 ± 0.23 c C	4.83 ± 0.20 c B
Transbond™ XT	ND (Non-detectable) c A	ND c A	ND c A	ND c A	ND d A

The same small letters in a column indicate no statistically significant difference in means.

The same large letters in a row indicate no statistically significant difference in means.

* - Indicates number of days since initial fabrication of the samples.

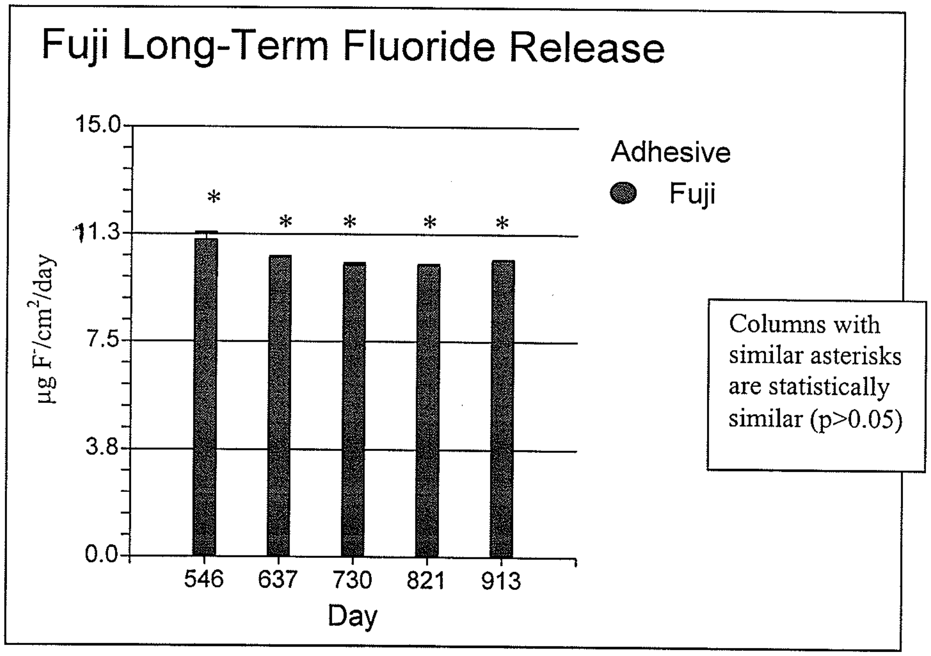
( ) – Parentheses indicate corresponding months since initial fabrication of samples.

4.1.2 Fuji Ortho™ LC Fluoride Release Rates

Fuji Ortho™ LC released statistically similar levels of fluoride at all time points (days 546, 637, 730, 821 and 913) ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Fuji Ortho™ LC are found in Table 2 and Figure 28.

Table 2: Fuji Ortho™ LC long-term fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
546	Fuji Ortho™ LC	5	11.04	0.27
637	Fuji Ortho™ LC	5	10.45	0.040
730	Fuji Ortho™ LC	5	10.18	0.071
821	Fuji Ortho™ LC	5	10.15	0.052
913	Fuji Ortho™ LC	5	10.33	0.031



Columns with similar asterisks are statistically similar ($p>0.05$)

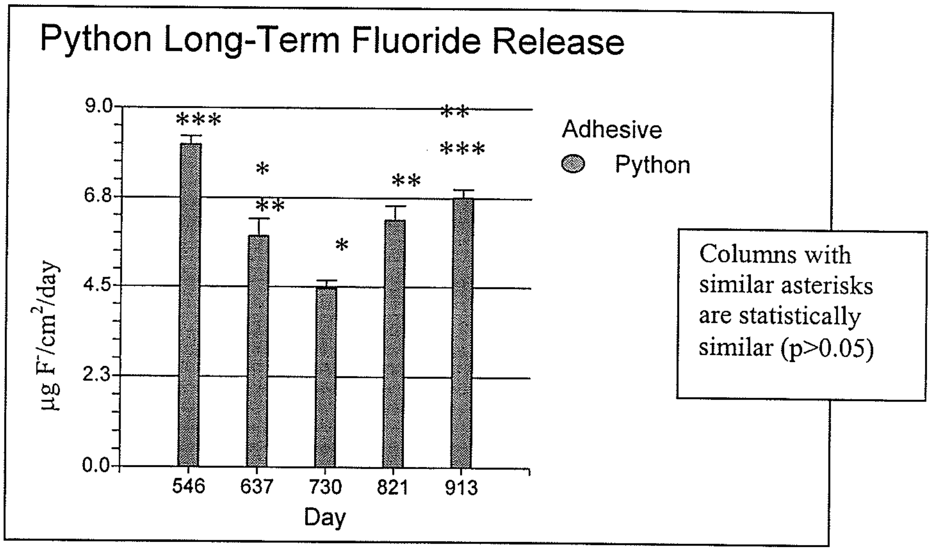
Figure 28: Fuji Ortho™ LC long-term fluoride release rates. Error bars indicate standard error.

4.1.3 Python™ Fluoride Release Rates

Python™ released 8.09 ± 0.21 µg F$^-$/cm^2/day on day 546, followed by a statistically significant decrease to levels of 5.79 ± 0.43 µg F$^-$/cm^2/day on day 637 and 4.47 ± 0.20 µg F$^-$/cm^2/day on day 730 ($p<0.0001$). This was followed a statistically significant increase ($p<0.0001$) in fluoride release to 6.19 ± 0.36 µg F$^-$/cm^2/day on day 821 and 6.77 ± 0.21 µg F$^-$/cm^2/day on day 913. The fluoride release values on days 821 and 913 were statistically similar ($p>0.05$), but only day 913 had fluoride release values similar to the initial measurement on day 546 ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Python™ are found in Table 3 and Figure 29.

Table 3: Python™ long-term fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (µg F$^-$/cm^2/day)	SE (µg F$^-$/cm^2/day)
546	Python™	5	8.09	0.21
637	Python™	5	5.79	0.43
730	Python™	5	4.47	0.20
821	Python™	5	6.19	0.36
913	Python™	5	6.77	0.21



Columns with similar asterisks are statistically similar ($p>0.05$)

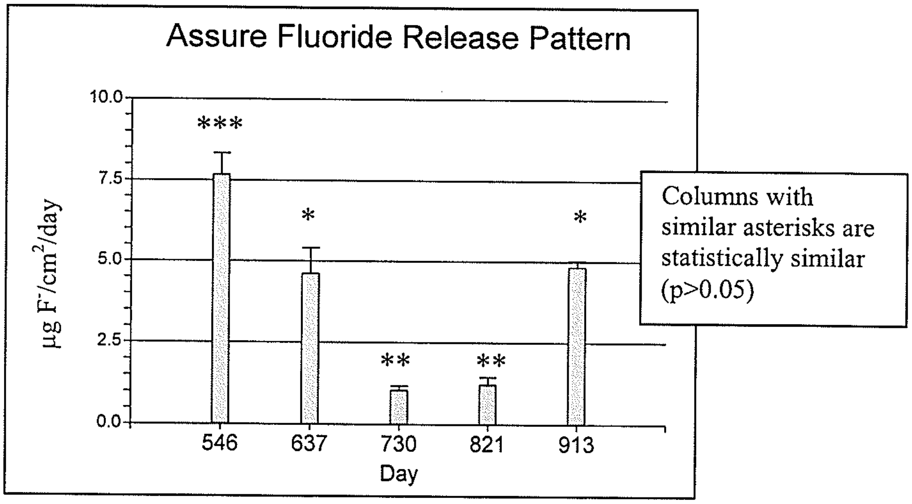
Figure 29: Python™ long-term fluoride release rates. Error bars indicate standard error.

4.1.4 Assure™ Fluoride Release Rates

Assure™ showed statistically significant decreases in fluoride release levels from 7.68 ± 0.65 µg F^-/cm^2/day (day 546) to 4.62 ± 0.79 µg F^-/cm^2/day (day 637) and from 4.62 ± 0.79 µg F^-/cm^2/day (day 637) to 1.04 ± 0.14 µg F^-/cm^2/day (day 730) ($p<0.001$). Fluoride release levels of Assure™ were statistically similar on day 730 (1.04 ± 0.14 µg F^-/cm^2/day) and day 821 (1.21 ± 0.23 µg F^-/cm^2/day) ($p>0.05$). There was a statistically significant increase in fluoride release from day 821 to day 913 (4.83 ± 0.20 µg F^-/cm^2/day) ($p<0.001$) to a level similar to day 637 ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Assure™ are found in Table 4 and Figure 30.

Table 4: Assure™ long-term fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release (µg F^-/cm^2/day)	SE (µg F^-/cm^2/day)
546	Assure™	5	7.68	0.65
637	Assure™	5	4.62	0.79
730	Assure™	5	1.04	0.14
821	Assure™	5	1.21	0.23
913	Assure™	5	4.83	0.20



Columns with similar asterisks are statistically similar (p>0.05)

Figure 30: Assure™ long-term fluoride release rates. Error bars indicate standard error.

4.1.5 Transbond™ XT Fluoride Release Rates

Transbond™ XT did not release detectable levels of fluoride at any point during the measurement period. Descriptive statistics of mean fluoride release rates and standard errors for Transbond™ XT are found in Table 5 and Figure 31.

Table 5: Transbond™ XT long-term fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release ($\mu g\ F^-/cm^2/day$)	SE ($\mu g\ F^-/cm^2/day$)
546	Transbond™ XT	5	ND	ND
637	Transbond™ XT	5	ND	ND
730	Transbond™ XT	5	ND	ND
821	Transbond™ XT	5	ND	ND
913	Transbond™ XT	5	ND	ND

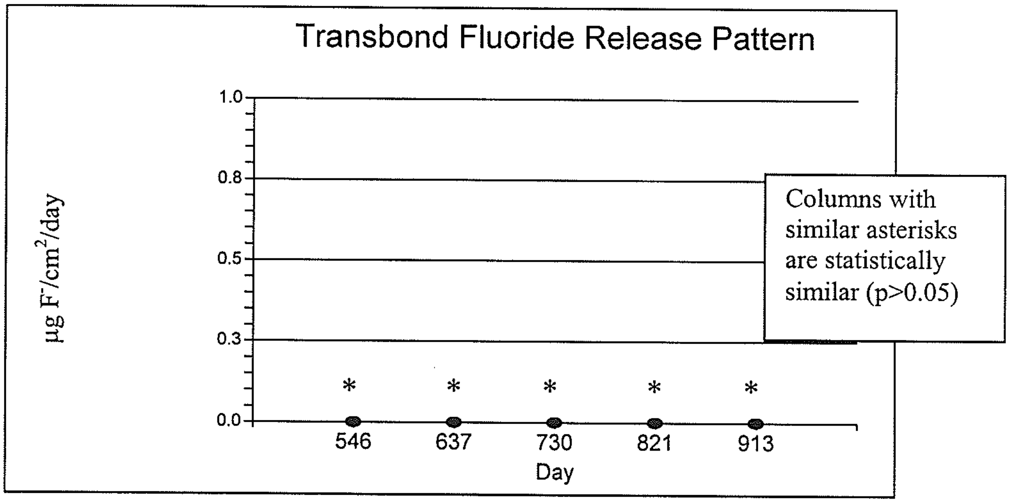


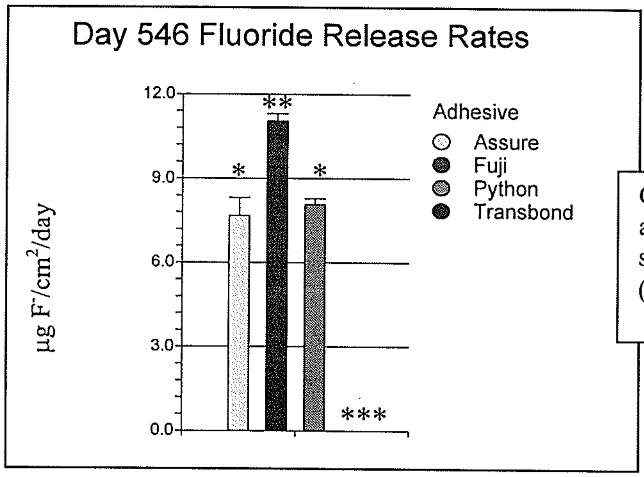
Figure 31: Transbond™ XT long-term fluoride release rates. Error bars indicate standard error.

4.1.6 Day 546 Fluoride Release Rates

The highest mean fluoride release was from the Fuji Ortho™ LC samples (11.04 ± 0.27 μg F^-/cm^2/day). Its mean fluoride release was significantly higher ($p<0.0001$) than those for the other sample groups on day 546. Python™ (8.09 ± 0.21 μg F^-/cm^2/day) and Assure™ (7.68 ± 0.65 μg F^-/cm^2/day) showed no significant difference in their fluoride release levels ($p>0.05$). Transbond™ XT had no detectable fluoride release and was significantly lower than all other groups ($p<0.0001$). Descriptive statistics of mean fluoride release rates and standard errors for day 546 are found in Table 6 and Figure 32.

Table 6: Day 546 fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
546	Assure™	5	7.68	0.65
546	Fuji Ortho™ LC	5	11.04	0.27
546	Python™	5	8.09	0.21
546	Transbond™ XT	5	Not Detectable (ND)	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

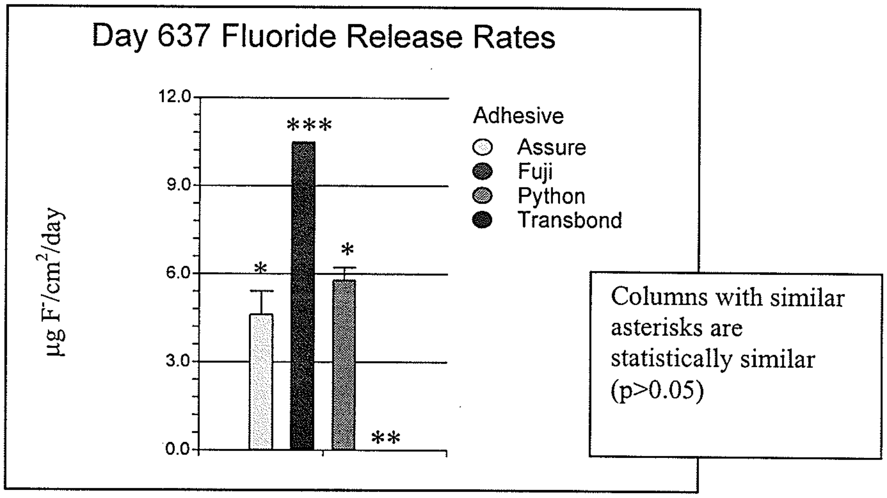
Figure 32: Day 546 fluoride release rates. Error bars indicate standard error.

4.1.7 Day 637 Fluoride Release Rates

The highest mean fluoride release value was from the Fuji Ortho™ LC samples (10.45 ± 0.040 μg F^-/cm^2/day). This was significantly higher ($p<0.0001$) than all other groups on day 637. Python™ released 5.79 ± 0.43 μg F^-/cm^2/day, which was slightly higher, but statistically similar to the 4.62 ± 0.79 μg F^-/cm^2/day released by Assure™ ($p>0.05$). Transbond™ XT did not release detectable levels of fluoride, and was significantly lower than all other groups on day 637 ($p<0.0001$). Descriptive statistics of mean fluoride release rates and standard errors for day 637 are found in Table 7 and Figure 33.

Table 7: Day 637 fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
637	Assure™	5	4.62	0.79
637	Fuji Ortho™ LC	5	10.45	0.040
637	Python™	5	5.79	0.43
637	Transbond™ XT	5	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

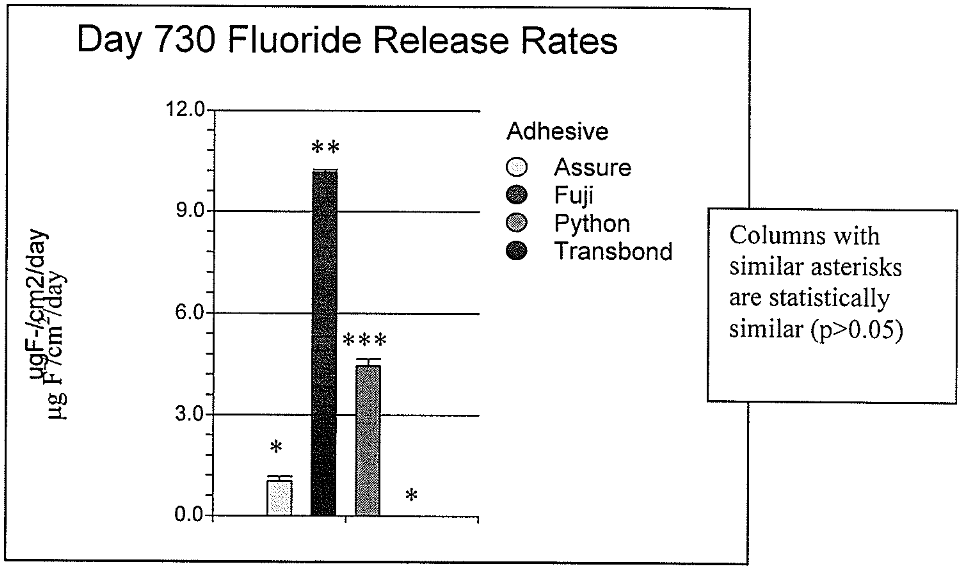
Figure 33: Day 637 fluoride release rates. Error bars indicate standard error.

4.1.8 Day 730 Fluoride Release Rates

On day 730, the fluoride release rate from Fuji Ortho™ LC (10.18 ± 0.071 μg F$^-$/cm^2/day) was significantly higher than the Python™ fluoride release rate (4.47 ± 0.20 μg F$^-$/cm^2/day) ($p<0.0001$). Release from Python™ was significantly higher than from Assure™ (1.04 ± 0.14 μg F$^-$/cm^2/day) and Transbond™ XT (non-detectable) ($p<0.0001$), which were statistically similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 730 are found in Table 8 and Figure 34.

Table 8: Day 730 fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F$^-$/cm^2/day)	SE (μg F$^-$/cm^2/day)
730	Assure™	5	1.04	0.14
730	Fuji Ortho™ LC	5	10.18	0.071
730	Python™	5	4.47	0.20
730	Transbond™ XT	5	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

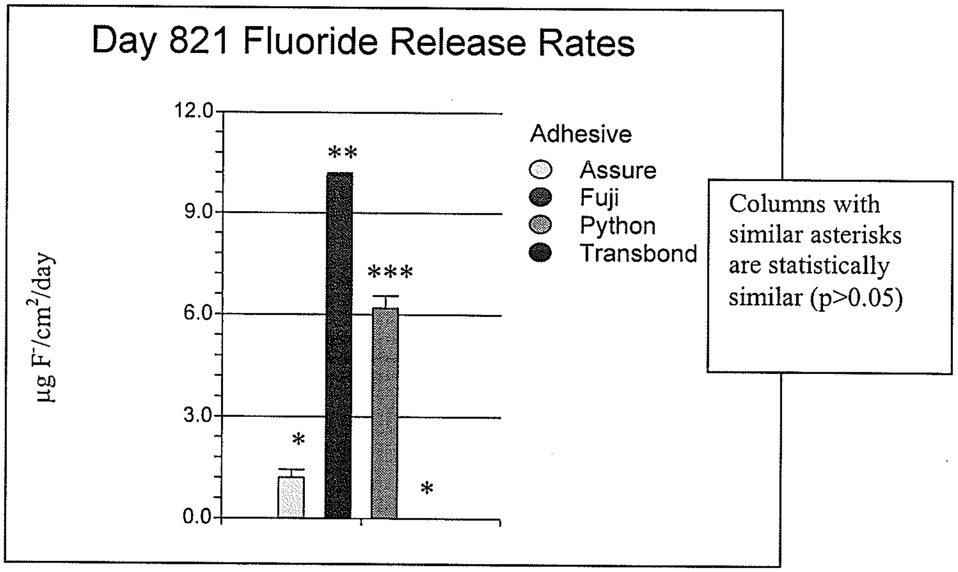
Figure 34: Day 730 fluoride release rates. Error bars indicate standard error.

4.1.9 Day 821 Fluoride Release Rates

On day 821, the highest mean fluoride release rate was from Fuji Ortho™ LC (10.15 ± 0.052 μg F^{-}/cm^{2}/day), which was significantly higher than the other groups ($p<0.0001$). Python™ (6.19 ± 0.36 μg F^{-}/cm^{2}/day) had a mean fluoride release rate significantly higher ($p<0.0001$) than Assure™ (1.21 ± 0.23 μg F^{-}/cm^{2}/day) and Transbond™ XT (non-detectable), which were statistically similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 821 are found in Table 9 and Figure 35.

Table 9: Day 821 fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^{-}/cm^{2}/day)	SE (μg F^{-}/cm^{2}/day)
821	Assure™	5	1.21	0.23
821	Fuji Ortho™ LC	5	10.15	0.052
821	Python™	5	6.19	0.36
821	Transbond™ XT	5	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

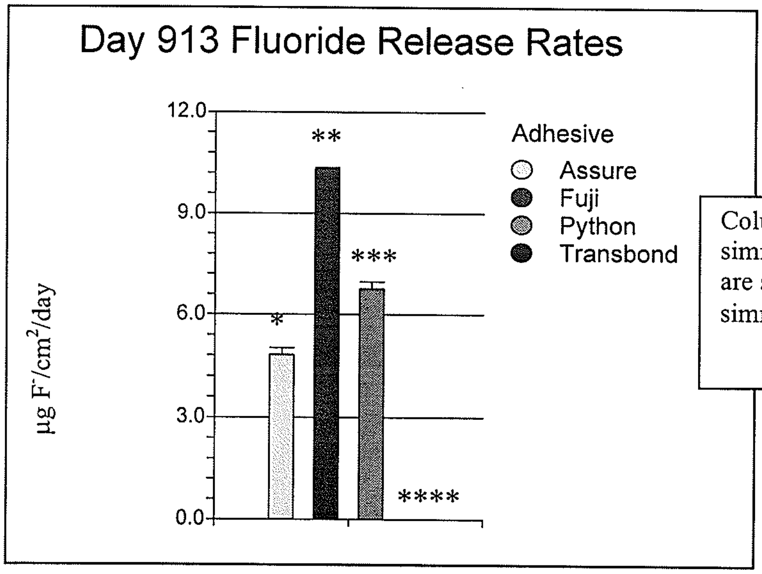
Figure 35: Day 821 fluoride release rates. Error bars indicate standard error.

4.1.10 Day 913 Fluoride Release Rates

All groups had significantly different fluoride release rates on day 913 ($p<0.0001$). Fuji Ortho™ LC had the highest fluoride release rate (10.33 ± 0.031 μg F^{-}/cm^{2}/day), followed by Python™ (6.77 ± 0.21 μg F^{-}/cm^{2}/day), Assure™ (4.83 ± 0.20 μg F^{-}/cm^{2}/day) and Transbond™ XT (non-detectable fluoride release rate). Descriptive statistics of mean fluoride release rates and standard errors for day 913 are found in Table 10 and Figure 36.

Table 10: Day 913 fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^{-}/cm^{2}/day)	SE (μg F^{-}/cm^{2}/day)
913	Assure™	5	4.83	0.20
913	Fuji Ortho™ LC	5	10.33	0.031
913	Python™	5	6.77	0.21
913	Transbond™ XT	5	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

Figure 36: Day 913 fluoride release rates. Error bars indicate standard error.

4.2 Fluoride Release from Samples Re-exposed to Fluoride

4.2.1 Overall Pattern

All materials showed a decrease in fluoride release following the first day of post-fluoride exposure. On all days except day 546, Fuji Ortho™ LC released the most fluoride, followed in decreasing order by Python™ > Assure™ > Transbond™ XT. On day 546, Fuji Ortho™ LC released the most fluoride, followed by Assure™ > Python™ > Transbond™ XT. The overall pattern of fluoride release for all materials can be seen in Table 11. The fluoride release measurements for individual samples are found in Appendix 2.

Table 11: Fluoride re-release rates following fluoride exposure (mean ± S.E., n=5)

Material	Fluoride Release (µg/cm^2/day)							
	Day 546* (1 day)**	Day 548 (3 days)	Day 552 (7 days)	Day 575 (1 month)	Day 637 (3 months)	Day 730 (6 months)	Day 821 (9 months)	Day 913 (12 months)
Fuji Ortho™ LC	92.34 ± 1.48 a A	12.57 ± 2.18 a B	9.51 ± 0.099 a B	10.06 ± 0.072 a B	10.14 ± 0.064 a B	10.06 ± 0.043 a B	10.20 ± 0.043 a B	10.33 ± 0.020 a B
Python™	36.60 ± 5.19 b A	5.85 ± 0.36 a b B	1.87 ± 0.33 b B	3.68 ± 0.38 a b B	5.79 ± 0.22 a b B	5.40 ± 0.18 a b B	6.68 ± 0.39 a b B	7.23 ± 0.24 a b B
Assure™	63.40 ± 4.68 c A	2.90 ± 0.88 b B	0.66 ± 0.085 b B	0.86 ± 0.16 b B	3.27 ± 0.64 a b B	1.28 ± 0.24 b B	1.20 ± 0.19 b B	4.40 ± 0.46 a b B
Transbond™ XT	5.94 ± 1.24 d A	0.043 ± 0.043 b A	ND b A	0.021 ± 0.021 b A	0.026 ± 0.026 b A	ND b A	ND b A	ND b A

The same small letters in a column indicate no statistically significant difference in means.

The same large letters in a row indicate no statistically significant difference in means.

* - Indicates number of days since initial fabrication of the samples.

** - Indicates number of days following exposure to fluoride.

4.2.2 Fuji Ortho™ LC Fluoride Re-Release Rates

Fluoride release was highest on day 546 (92.34 ± 1.48 $\mu g\ F^-/cm^2/day$), immediately following fluoride exposure. This was significantly higher than at all other time points ($p<0.0001$) and decreased to 12.57 ± 2.18 $\mu g\ F^-/cm^2/day$ on day 548. The fluoride release was not significantly different on days 548, 552, 575, 637, 730, 821 and 913 ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Fuji Ortho™ LC are found in Table 12 and Figure 37.

Table 12: Fuji Ortho™ LC fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release ($\mu g\ F^-/cm^2/day$)	SE ($\mu g\ F^-/cm^2/day$)
546	Fuji Ortho™ LC	5	92.34	1.48
548	Fuji Ortho™ LC	5	12.57	2.18
552	Fuji Ortho™ LC	5	9.51	0.099
575	Fuji Ortho™ LC	5	10.06	0.072
637	Fuji Ortho™ LC	5	10.14	0.064
730	Fuji Ortho™ LC	5	10.06	0.043
821	Fuji Ortho™ LC	5	10.20	0.043
913	Fuji Ortho™ LC	5	10.33	0.020

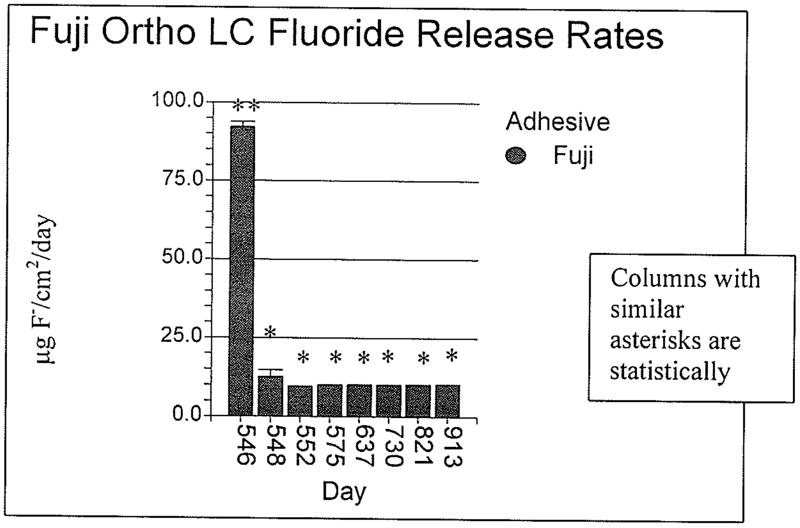


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Figure 37: Fuji Ortho™ LC fluoride re-release rates. Error bars indicate standard error.

4.2.3 Python™ Fluoride Re-Release Rates

Python™ released 36.60 ± 5.19 µg F$^-$/cm^2/day, which was significantly more than at any other time point ($p<0.0001$). On days 548, 552, 575, 637, 730, 821 and 913, Python™ had statistically similar fluoride release rates ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Python™ are found in Table 13 and Figure 38.

Table 13: Python™ fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (µg F$^-$/cm^2/day)	SE (µg F$^-$/cm^2/day)
546	Python™	5	36.60	5.19
548	Python™	5	5.85	0.36
552	Python™	5	1.87	0.33
575	Python™	5	3.68	0.38
637	Python™	5	5.79	0.22
730	Python™	5	5.40	0.18
821	Python™	5	6.68	0.39
913	Python™	5	7.23	0.24

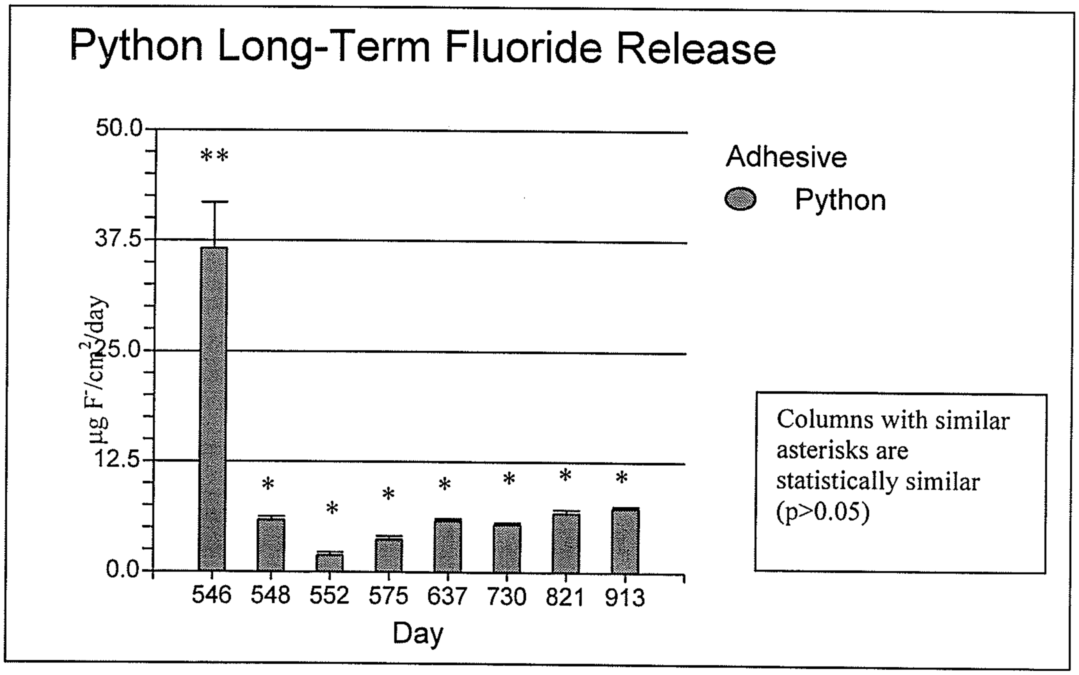


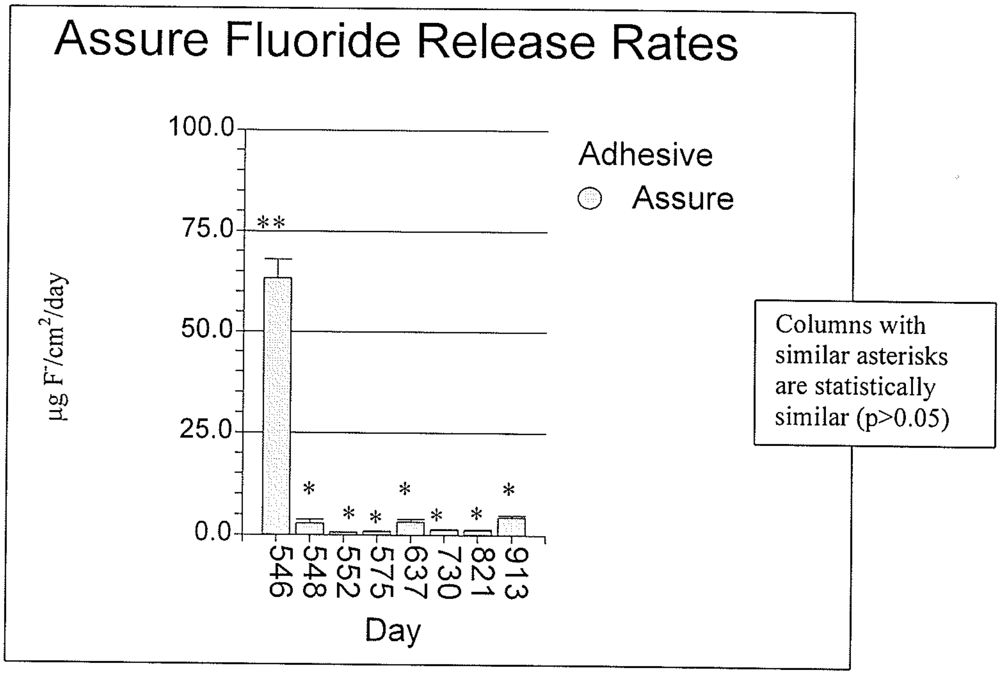
Figure 38: Python™ fluoride re-release rates. Error bars indicate standard error.

4.2.4 Assure™ Fluoride Re-Release Rates

Assure™ had a significantly higher fluoride release rate on day 546 (63.40 ± 4.68 μg F^-/cm^2/day) than at any other time point ($p<0.0001$). The fluoride release rates on days 548, 552, 575, 637, 730, 821 and 913 were statistically similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Assure™ are found in Table 14 and Figure 39.

Table 14: Assure™ fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
546	Assure™	5	63.40	4.68
548	Assure™	5	2.90	0.88
552	Assure™	5	0.66	0.085
575	Assure™	5	0.86	0.16
637	Assure™	5	3.27	0.64
730	Assure™	5	1.28	0.24
821	Assure™	5	1.20	0.19
913	Assure™	5	4.40	0.46



Columns with similar asterisks are statistically similar ($p>0.05$)

Figure 39: Assure™ fluoride re-release rates. Error bars indicate standard error.

4.2.5 Transbond™ XT Fluoride Re-Release Rates

The highest fluoride release rate for Transbond™ XT was on day 546 (5.94 ± 1.24 μg F^-/cm^2/day). Detectable fluoride release rates were also seen on day 548 (0.043 ± 0.043 μg F^-/cm^2/day), day 575 (0.021 ± 0.021 μg F^-/cm^2/day) and day 637 (0.026 ± 0.026 μg F^-/cm^2/day). On the remaining days fluoride release was non-detectable. However, at all time points the fluoride release rates were statistically similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Transbond™ XT are found in Table 15 and Figure 40.

Table 15: Transbond™ XT fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
546	Transbond™ XT	5	5.94	1.24
548	Transbond™ XT	5	0.043	0.043
552	Transbond™ XT	5	ND	ND
575	Transbond™ XT	5	0.021	0.021
637	Transbond™ XT	5	0.026	0.026
730	Transbond™ XT	5	ND	ND
821	Transbond™ XT	5	ND	ND
913	Transbond™ XT	5	ND	ND

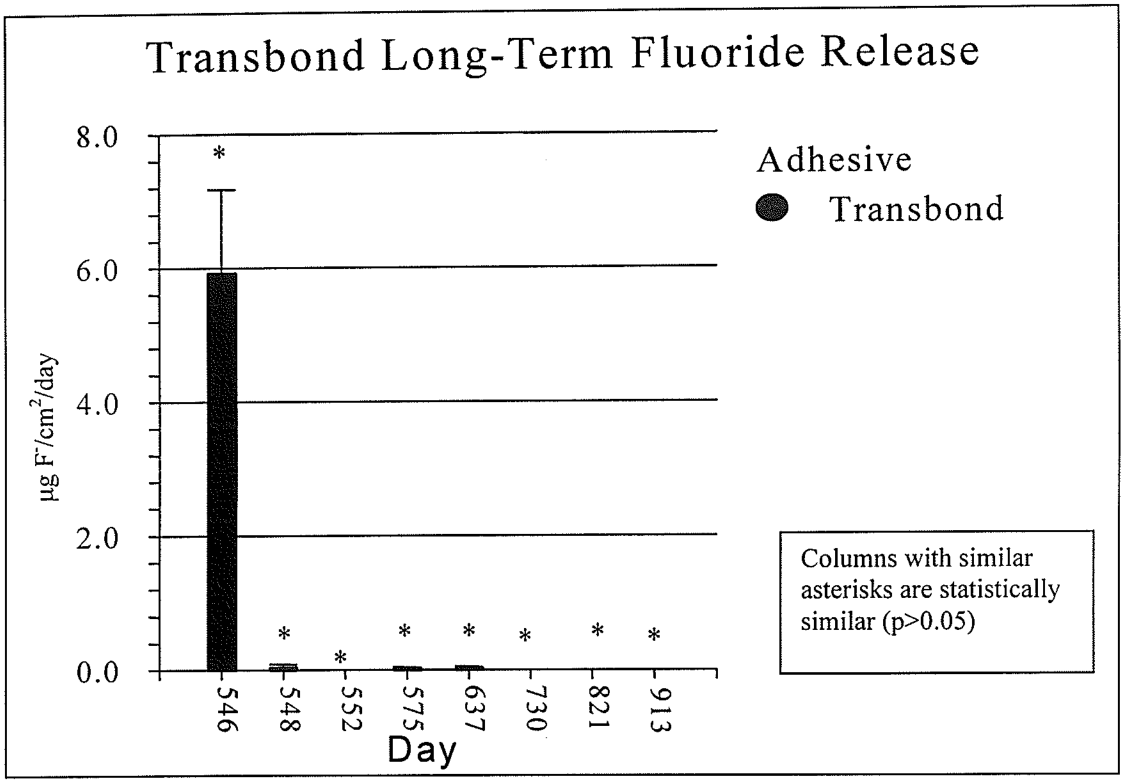


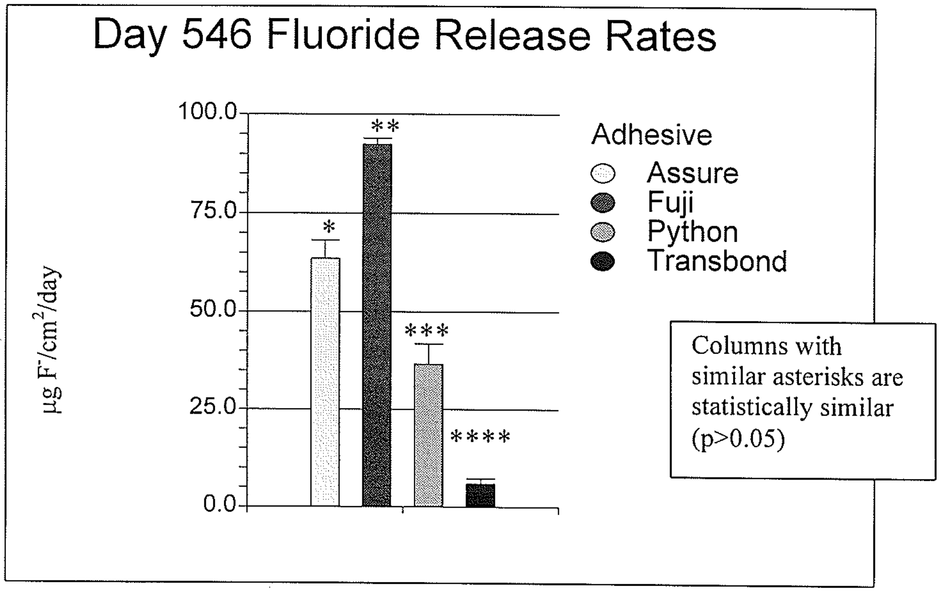
Figure 40: Transbond™ XT fluoride re-release rates. Error bars indicate standard error.

4.2.6 Day 546 Fluoride Re-release Rates

The fluoride release rates for each of the materials were significantly different on day 546 ($p<0.0001$). Fuji Ortho™ LC had the highest fluoride release rate (92.34 ± 1.48 $\mu g\ F^-/cm^2/day$), followed by Assure™ (63.40 ± 4.68 $\mu g\ F^-/cm^2/day$), Python™ (36.60 ± 5.19 $\mu g\ F^-/cm^2/day$) and Transbond™ XT (5.94 ± 1.24 $\mu g\ F^-/cm^2/day$). Descriptive statistics of mean fluoride release rates and standard errors for day 546 are found in Table 16 and Figure 41.

Table 16: Day 546 fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F$^-$/cm^2/day)	SE (μg F$^-$/cm^2/day)
546	Fuji Ortho™ LC	5	92.34	1.48
546	Python™	5	36.60	5.19
546	Assure™	5	63.40	4.68
546	Transbond™ XT	5	5.94	1.24


Day 546 Fluoride Release Rates

Columns with similar asterisks are statistically similar (p>0.05)

Figure 41: Day 546 fluoride re-release rates. Error bars indicate standard error.

4.2.7 Day 548 Fluoride Re-release Rates

Fuji Ortho™ LC had the highest fluoride release rate (12.57 ± 2.18 μg F$^-$/cm^2/day), which was statistically similar to the fluoride release rate of Python™ (5.85 ± 0.36 μg F$^-$/cm^2/day) ($p>0.05$), but significantly higher than Assure™ (2.90 ± 0.88 μg F$^-$/cm^2/day) and Transbond™ XT (0.043 ± 0.043 μg F$^-$/cm^2/day) ($p<0.0001$). However, the fluoride release rates of Python™, Assure™ and Transbond™ XT were statistically similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 546 are found in Table 17 and Figure 42.

Table 17: Day 548 fluoride re-release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release ($\mu g\ F^-/cm^2/day$)	SE ($\mu g\ F^-/cm^2/day$)
548	Fuji Ortho™ LC	5	12.57	2.18
548	Python™	5	5.85	0.36
548	Assure™	5	2.90	0.88
548	Transbond™ XT	5	0.043	0.043

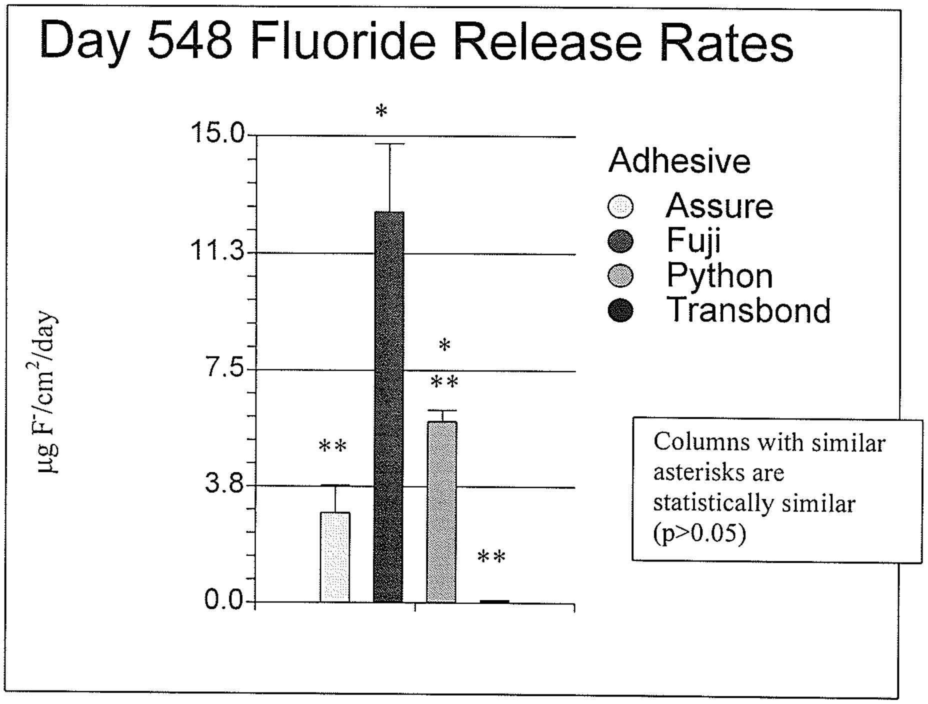


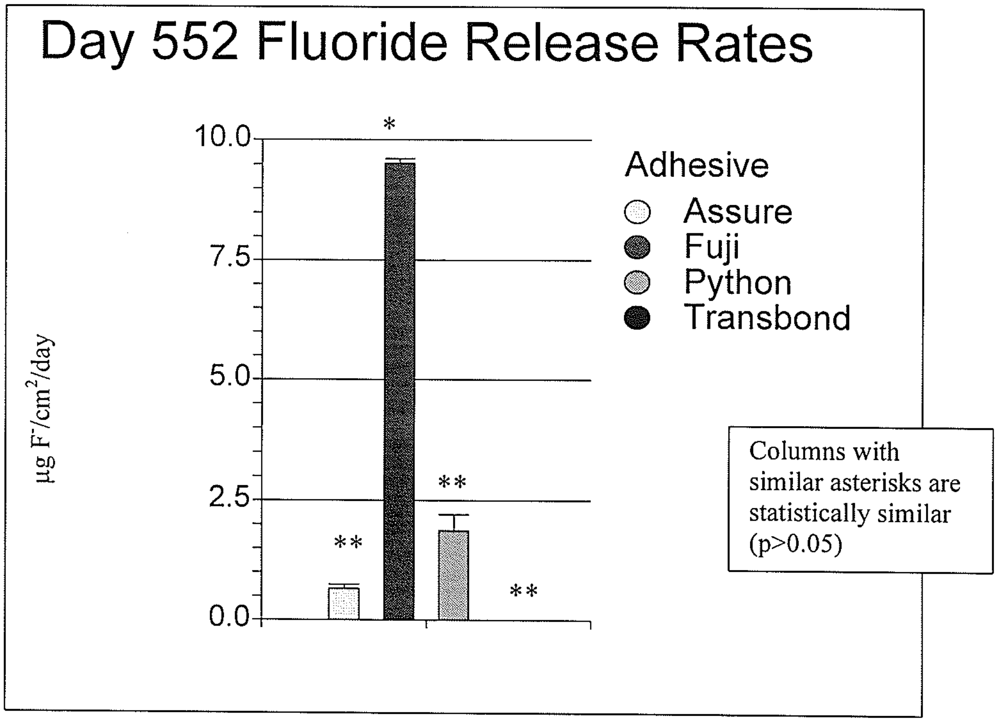
Figure 42: Day 548 fluoride re-release rates. Error bars indicate standard error.

4.2.8 Day 552 Fluoride Re-release Rates

Fuji Ortho™ LC had a significantly higher fluoride release rate (9.51 ± 0.099 $\mu g\ F^-/cm^2/day$) than all the other groups ($p<0.0001$). Python™, Assure™ and Fuji Ortho™ LC had similar fluoride release rates on day 552 ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 552 are found in Table 18 and Figure 43.

Table 18: Day 552 fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F$^-$/cm^2/day)	SE (μg F$^-$/cm^2/day)
552	Fuji Ortho™ LC	5	9.51	0.099
552	Python™	5	1.87	0.33
552	Assure™	5	0.66	0.085
552	Transbond™ XT	5	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

Figure 43: Day 552 fluoride re-release rates. Error bars indicate standard error.

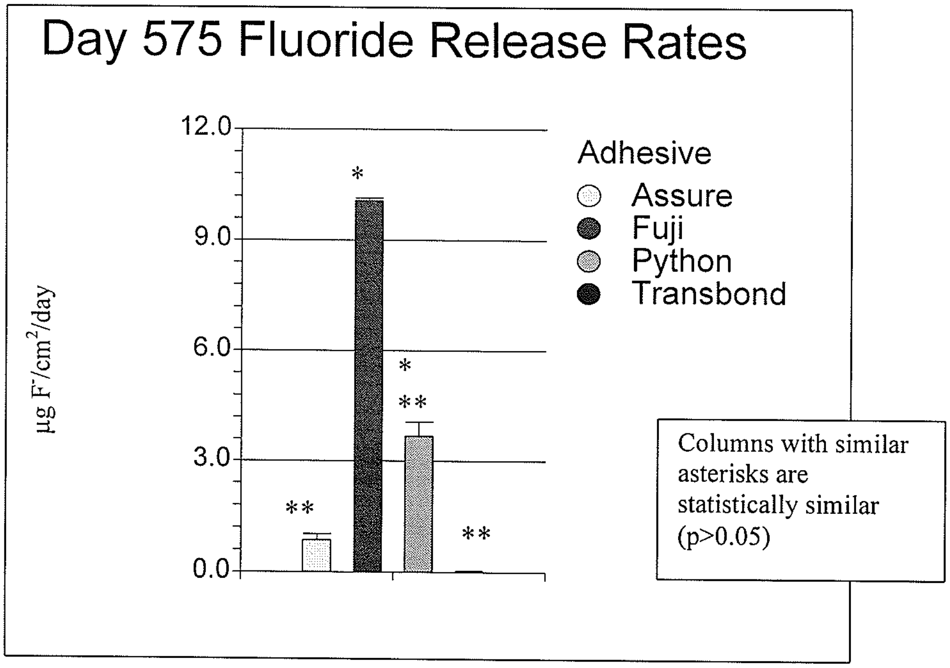
4.2.9 Day 575 Fluoride Re-release Rates

Fuji Ortho™ LC had the highest fluoride release rate on day 575 (10.06 ± 0.072 μg F$^-$/cm^2/day). Python™ had a lower fluoride release rate of 3.68 ± 0.38 μg F$^-$/cm^2/day, but was statistically similar to Fuji Ortho™ LC ($p>0.05$). Statistically similar fluoride release rates were found for Assure™ (0.86 ± 0.16 μg F$^-$/cm^2/day) and Transbond™ XT (0.021 ± 0.021 μg F$^-$/cm^2/day) ($p>0.05$), and were significantly lower than Fuji Ortho™ LC ($p<0.0001$). Rates for Python™, Assure™ and Transbond™ XT were statistically similar

($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 575 are found in Table 19 and Figure 44.

Table 19: Day 575 fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release ($\mu g\ F^-/cm^2/day$)	SE ($\mu g\ F^-/cm^2/day$)
575	Fuji Ortho™ LC	5	10.06	0.072
575	Python™	5	3.68	0.38
575	Assure™	5	0.86	0.16
575	Transbond™ XT	5	0.021	0.021



Columns with similar asterisks are statistically similar ($p>0.05$)

Figure 44: Day 575 fluoride re-release rates. Error bars indicate standard error.

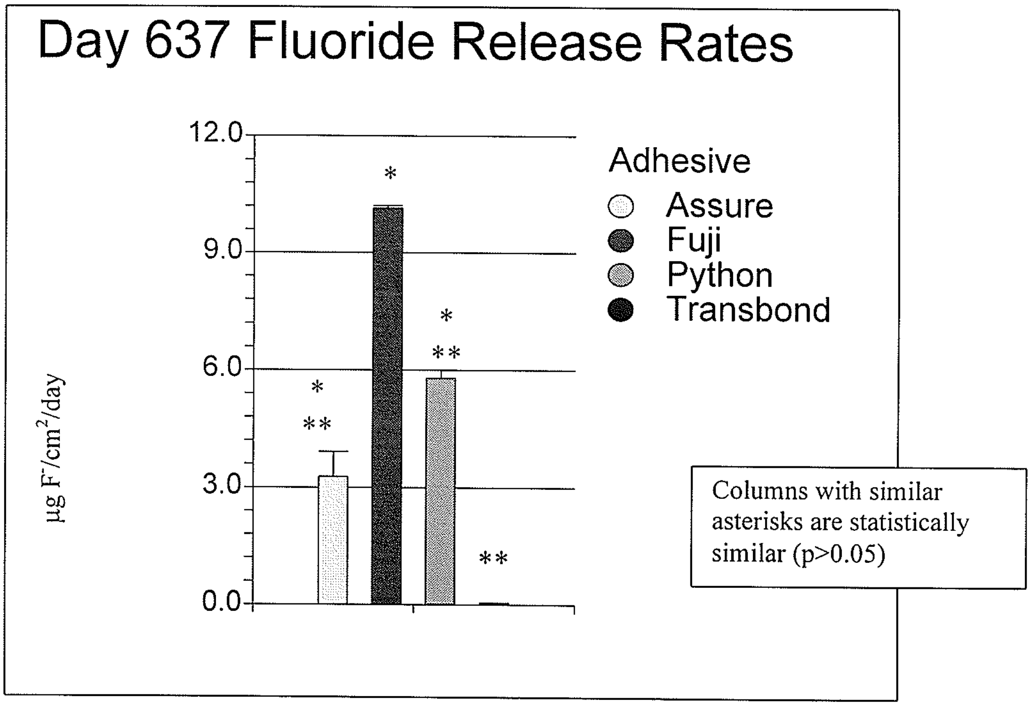
4.2.10 Day 637 Fluoride Re-release Rates

The fluoride release rates for Fuji Ortho™ LC (10.14 ± 0.064 $\mu g\ F^-/cm^2/day$) and Transbond™ XT (0.026 ± 0.026 $\mu g\ F^-/cm^2/day$) were significantly different ($p<0.0001$). The release rates for Fuji Ortho™ LC, Python™ (5.79 ± 0.22 $\mu g\ F^-/cm^2/day$) and Assure™

(3.27 ± 0.64 μg F^-/cm^2/day) were similar ($p>0.05$), and Python™, Assure™ and Transbond™ XT were similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors are found in Table 20 and Figure 45.

Table 20: Day 637 fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
637	Fuji Ortho™ LC	5	10.14	0.064
637	Python™	5	5.79	0.22
637	Assure™	5	3.27	0.64
637	Transbond™ XT	5	0.026	0.026



Columns with similar asterisks are statistically similar ($p>0.05$)

Figure 45: Day 637 fluoride re-release rates. Error bars indicate standard error.

4.2.11 Day 730 Fluoride Re-release Rates

The fluoride releases rate for Fuji Ortho™ LC (10.06 ± 0.043 μg F^-/cm^2/day) were significantly higher than those for Assure™ (1.28 ± 0.24 μg F^-/cm^2/day) and Transbond™

XT (ND) ($p<0.0001$). The fluoride release rate for Python™ was 5.40 ± 0.18 μg F^-/cm^2/day, which was statistically similar to all other groups ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 730 are found in Table 21 and Figure 46.

Table 21: Day 730 fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
730	Fuji Ortho™ LC	5	10.06	0.043
730	Python™	5	5.40	0.18
730	Assure™	5	1.28	0.24
730	Transbond™ XT	5	ND	ND

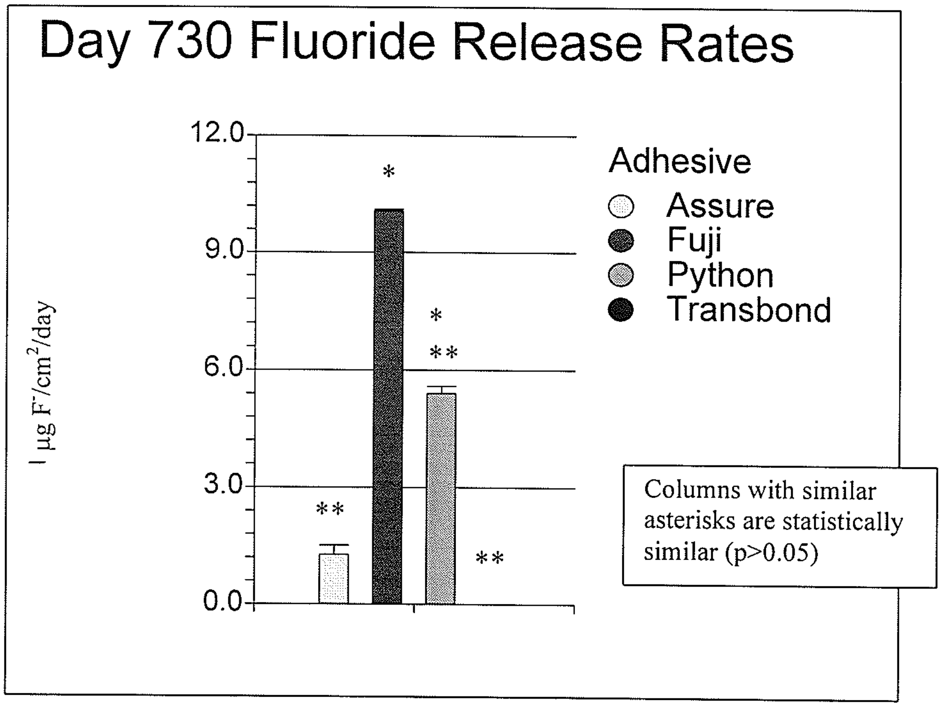


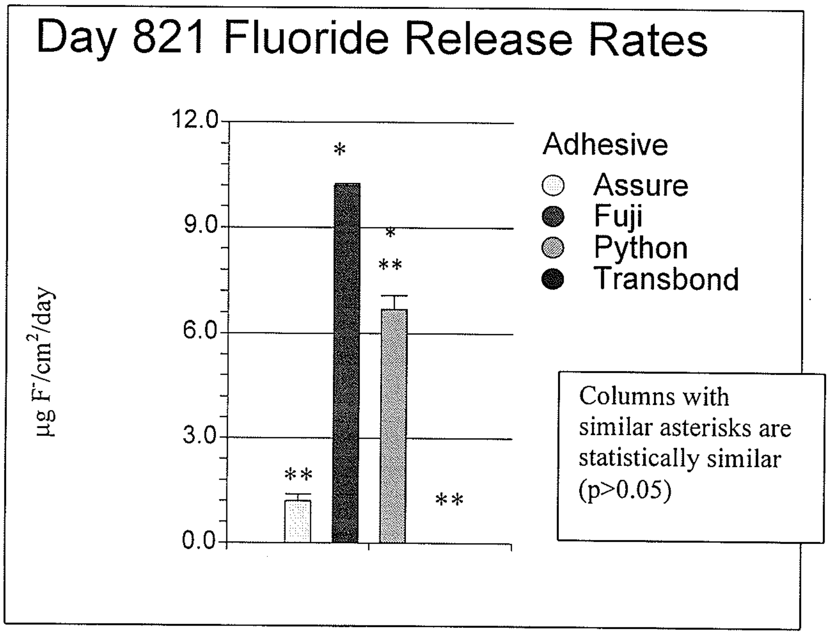
Figure 46: Day 730 fluoride re-release rates. Error bars indicate standard error.

4.2.12 Day 821 Fluoride Re-release Rates

The fluoride release rate for Fuji Ortho™ LC (10.20 ± 0.043 µg F^-/cm^2/day) was significantly higher than those for Assure™ (1.20 ± 0.19 µg F^-/cm^2/day) and Transbond™ XT (ND) ($p<0.0001$). The fluoride release rate for Python™ was 6.68 ± 0.39 µg F^-/cm^2/day, which was statistically similar to all other groups ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 821 are found in Table 22 and Figure 47.

Table 22: Day 821 fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (µg F^-/cm^2/day)	SE (µg F^-/cm^2/day)
821	Fuji Ortho™ LC	5	10.20	0.043
821	Python™	5	6.68	0.39
821	Assure™	5	1.20	0.19
821	Transbond™ XT	5	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

Figure 47: Day 821 fluoride re-release rates. Error bars indicate standard error.

4.2.13 Day 913 Fluoride Re-release Rates

The fluoride release rate for Fuji Ortho™ LC (10.33 ± 0.020 μg $F^-/cm^2/day$) was significantly higher than that of Transbond™ XT (ND) ($p<0.0001$). The fluoride release rate was 7.23 ± 0.24 μg $F^-/cm^2/day$ for Python™, and 4.40 ± 0.46 μg $F^-/cm^2/day$ for Assure™, neither of which were significantly different from any other group ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for day 913 are found in Table 23 and Figure 48.

Table 23: Day 913 fluoride re-release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg $F^-/cm^2/day$)	SE (μg $F^-/cm^2/day$)
913	Fuji Ortho™ LC	5	10.33	0.020
913	Python™	5	7.23	0.24
913	Assure™	5	4.40	0.46
913	Transbond™ XT	5	ND	ND

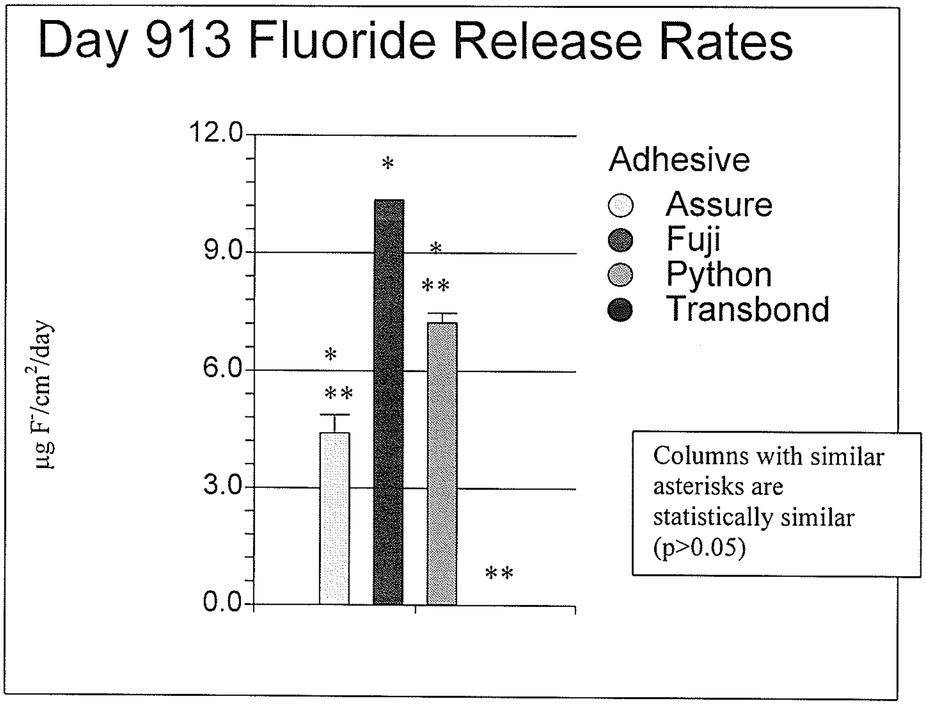


Figure 48: Day 913 fluoride re-release rates. Error bars indicate standard error.

4.3 Fluoride Release Rates from Tooth-Bracket Model

4.3.1 Overall Pattern

At all time points where detectable levels of fluoride were released, Assure™ had the highest fluoride release rates. Assure released fluoride on days 1, 3, 7 and 30; Quick Cure™ released fluoride only on day 1; and Transbond™ XT never released detectable levels of fluoride. All fluoride release rates were statistically similar ($p>0.05$) except for Assure™ on day 1 which was significantly higher ($p<0.0001$). The overall pattern of fluoride release for all materials can be seen in Table 24. The fluoride release measurements for individual samples can be found in Appendix 3.

Table 24: Fluoride release rates for tooth-bracket model (mean ± S.E., n=5)

Material	Fluoride Release (µg/cm^2/day)					
	Day 1*	Day 3	Day 7	Day 30	Day 90	Day 180
Assure™	236.39 ± 49.14 a A	41.59 ± 8.32 a B	14.49 ± 7.15 a B	3.03 ± 1.65 a B	ND a B	ND a B
Quick Cure™	10.45 ± 6.97 b A	ND a A	ND a A	ND a A	ND a A	ND a A
Transbond™ XT	ND b A	ND a A	ND a A	ND a A	ND a A	ND a A

The same small letters in a column indicate no statistically significant difference in means.

The same large letters in a row indicate no statistically significant difference in means.

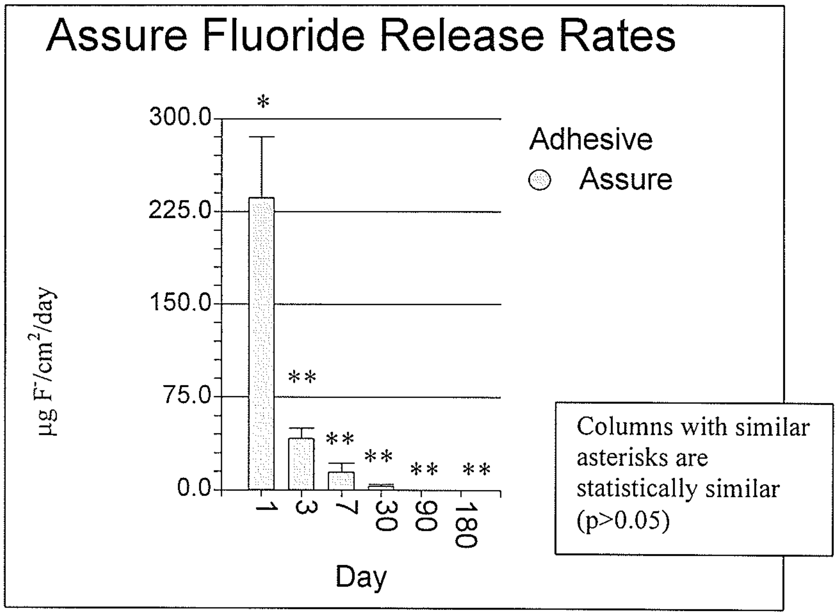
* - Indicates number of days since initial fabrication of the samples.

4.3.2 Assure™ Fluoride Release Rates

The fluoride release for Assure™ was highest on day 1 (236.39 ± 49.14 μg F^-/cm^2/day). This was followed by significant decrease to 41.59 ± 8.32 μg F^-/cm^2/day on day 3 ($p<0.0001$). The levels of fluoride release for all days after day 1 (including days 3, 7, 30, 90 and 180) were statistically similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Assure™ are found in Table 25 and Figure 49.

Table 25: Assure™ fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
1	Assure™	10	236.39	49.14
3	Assure™	10	41.59	8.32
7	Assure™	10	14.49	7.15
30	Assure™	10	3.03	1.65
90	Assure™	10	ND	ND
180	Assure™	10	ND	ND



Columns with similar asterisks are statistically similar (p>0.05)

Figure 49: Assure™ fluoride release rates. Error bars indicate standard error.

4.3.3 Quick Cure™ Fluoride Release Rates

Quick Cure™ released a detectable level of fluoride on day 1 only (10.45 ± 6.97 μg F^- /cm^2/day); all time points after that had non-detectable fluoride release rates. Statistically, however, all groups were similar ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors for Quick Cure™ are found in Table 26 and Figure 50.

Table 26: Quick Cure™ fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release (μg F^-/cm^2/day)	SE (μg F^-/cm^2/day)
1	Quick Cure™	10	10.45	6.97
3	Quick Cure™	10	ND	ND
7	Quick Cure™	10	ND	ND
30	Quick Cure™	10	ND	ND
90	Quick Cure™	10	ND	ND
180	Quick Cure™	10	ND	ND

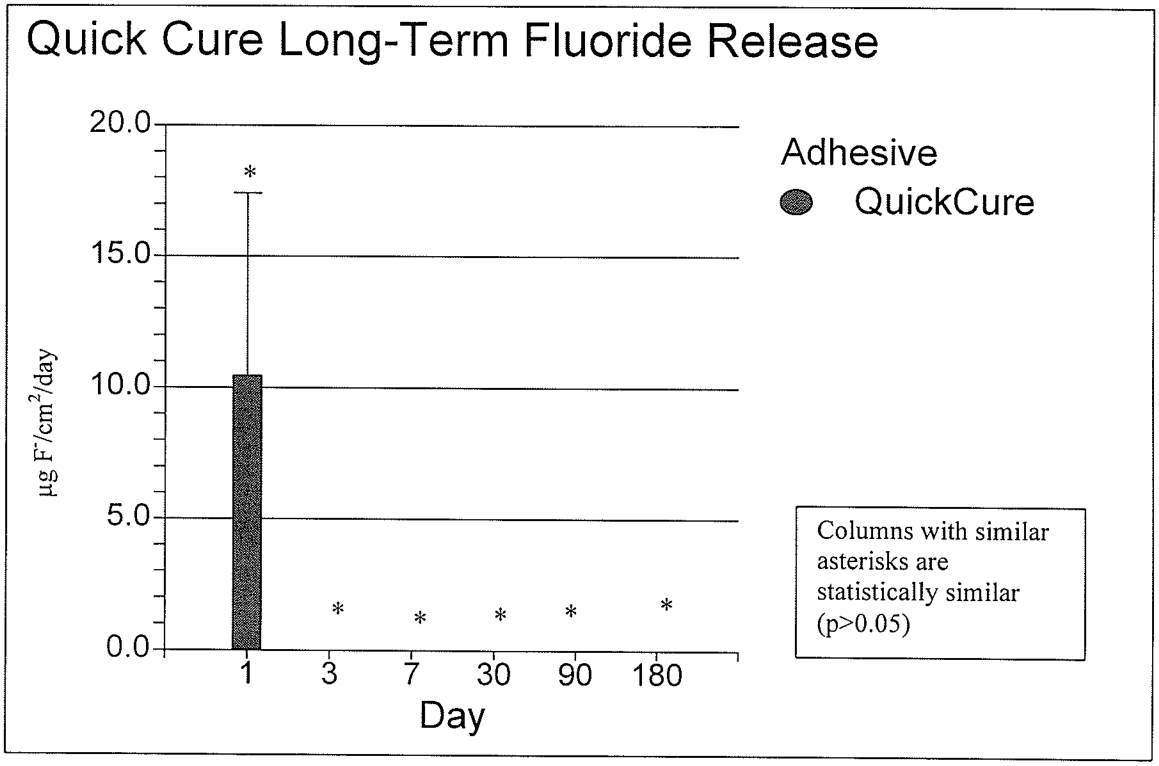


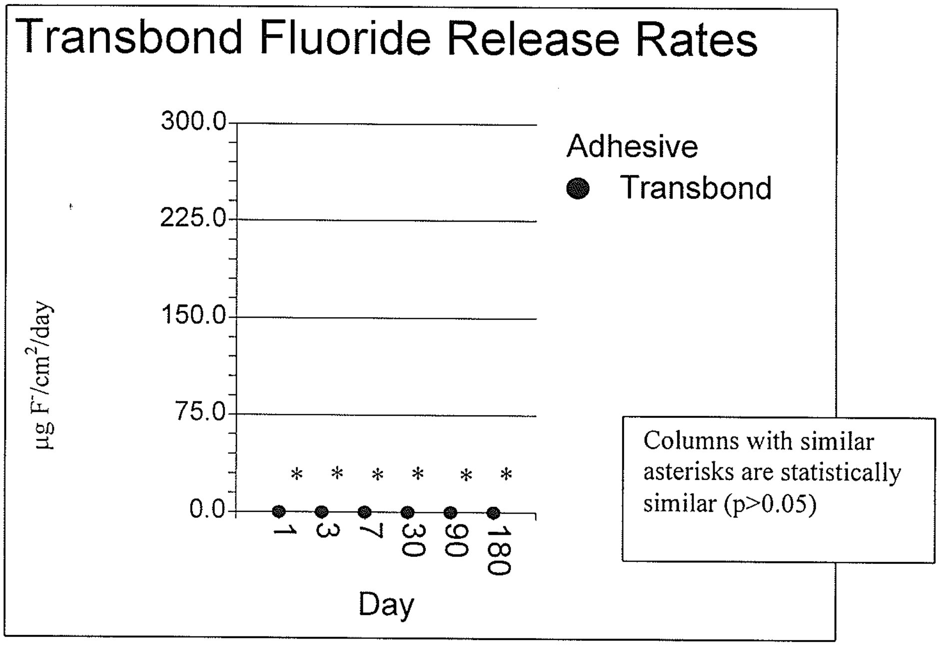
Figure 50: Quick Cure™ fluoride release rates. Error bars indicate standard error.

4.3.4 Transbond™ XT Fluoride Release Rates

Transbond™ XT did not release detectable levels of fluoride at any time point; therefore, all groups were statistically similar (p>0.05). Descriptive statistics of mean fluoride release rates and standard errors for Transbond™ XT are found in Table 27 and Figure 51.

Table 27: Transbond™ XT fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release (μg $F^-/cm^2/day$)	SE (μg $F^-/cm^2/day$)
1	Transbond™ XT	10	ND	ND
3	Transbond™ XT	10	ND	ND
7	Transbond™ XT	10	ND	ND
30	Transbond™ XT	10	ND	ND
90	Transbond™ XT	10	ND	ND
180	Transbond™ XT	10	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

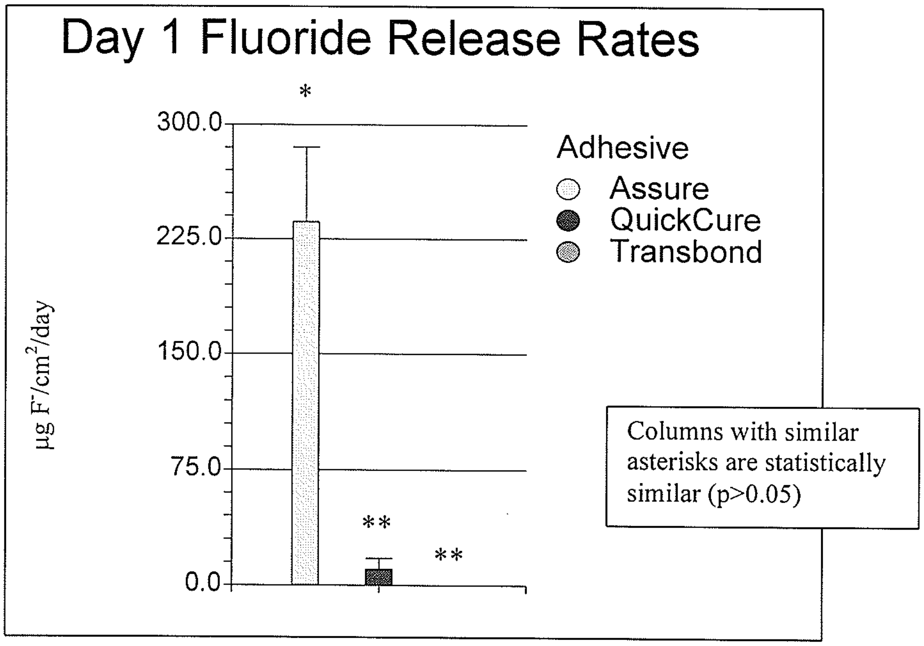
Figure 51: Transbond™ XT fluoride release rates. Error bars indicate standard error.

4.3.5 Day 1 Fluoride Release Rates

The fluoride release rate for Assure™ (236.39 ± 49.14 μg F^-/cm^2/day) was significantly more than those for all other groups ($p<0.0001$). Quick Cure™ had a fluoride release rate statistically similar to Transbond™ XT (p>0.05), which did not release detectable levels of fluoride. Descriptive statistics of mean fluoride release rates and standard errors for Transbond™ XT are found in Table 28 and Figure 51.

Table 28: Day 1 fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release (μg F$^-$/cm^2/day)	SE (μg F$^-$/cm^2/day)
1	Assure™	10	236.39	49.14
1	Quick Cure™	10	10.45	6.97
1	Transbond™ XT	10	ND	ND



Columns with similar asterisks are statistically similar (p>0.05)

Figure 52: Day 1 fluoride release rates. Error bars indicate standard error.

4.3.6 Day 3 Fluoride Release Rates

Assure™ had the only detectable fluoride release rate (41.59 ± 8.32 μg F$^-$/cm^2/day), but it was not significantly different from those of Quick Cure™ or Transbond™ XT (p>0.05).

Descriptive statistics of mean fluoride release rates and standard errors are found in Table 29 and Figure 53.

Table 29: Day 3 fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release (μg F$^-$/cm^2/day)	SE (μg F$^-$/cm^2/day)
3	Assure™	10	41.59	8.32
3	Quick Cure™	10	ND	ND
3	Transbond™ XT	10	ND	ND

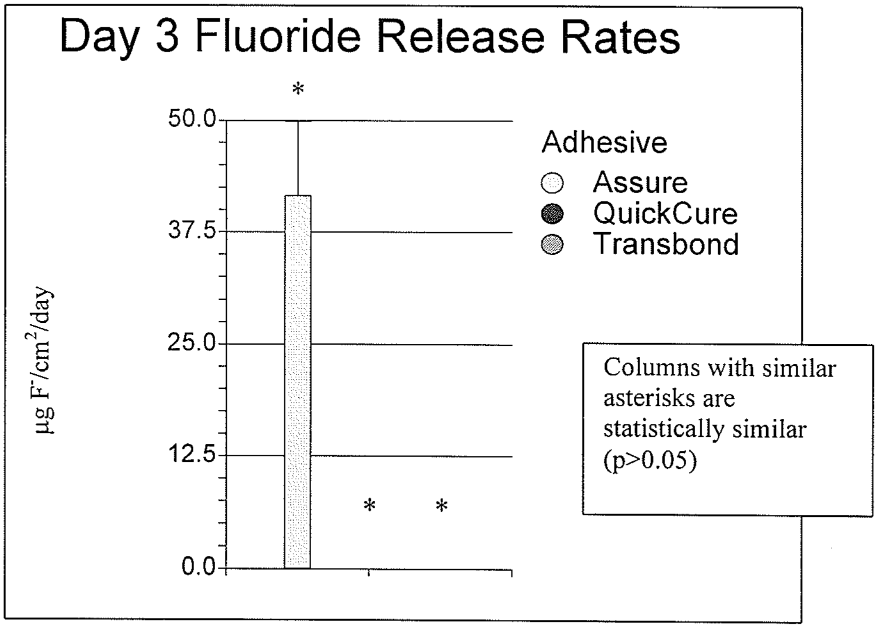


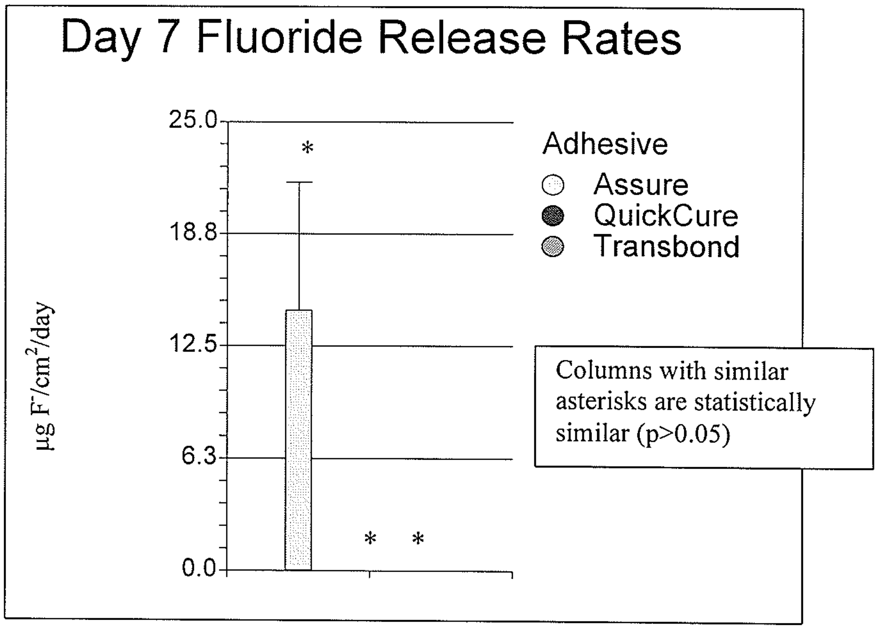
Figure 53: Day 3 fluoride release rates. Error bars indicate standard error.

4.3.7 Day 7 Fluoride Release Rates

Assure™ had a fluoride release rate of 14.49 ± 7.15 μg F$^-$/cm^2/day, while Quick Cure™ and Transbond™ XT did not release detectable levels of fluoride. All groups had statistically similar fluoride release rates ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors are found in Table 30 and Figure 54.

Table 30: Day 7 fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release (µg F^-/cm^2/day)	SE (µg F^-/cm^2/day)
7	Assure™	10	14.49	7.15
7	Quick Cure™	10	ND	ND
7	Transbond™ XT	10	ND	ND



Columns with similar asterisks are statistically similar (p>0.05)

Figure 54: Day 7 fluoride release rates. Error bars indicate standard error.

4.3.8 Day 30 Fluoride Release Rates

Assure™ had a fluoride release rate of 3.03 ± 1.65 µg F^-/cm^2/day, while Quick Cure™ and Transbond™ XT did not release detectable levels of fluoride. All groups had statistically similar rates of fluoride release ($p>0.05$). Descriptive statistics of mean fluoride release rates and standard errors are found in Table 31 and Figure 55.

Table 31: Day 30 fluoride release rate descriptive statistics

Day	Adhesive	N	Mean Fluoride Release ($\mu g\ F^-/cm^2/day$)	SE ($\mu g\ F^-/cm^2/day$)
30	Assure™	10	3.03	1.65
30	Quick Cure™	10	ND	ND
30	Transbond™ XT	10	ND	ND

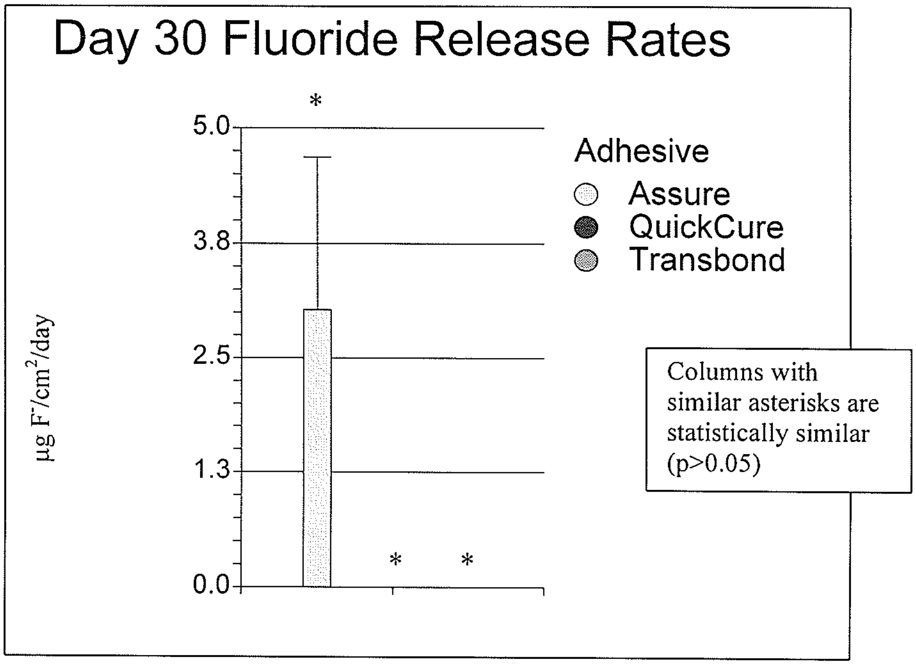


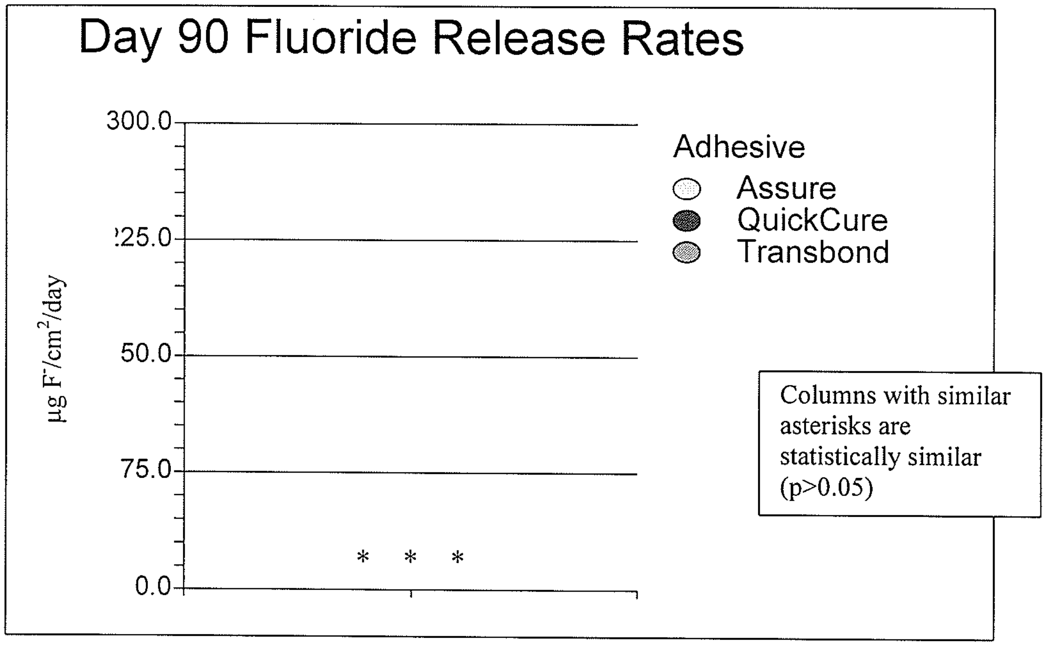
Figure 55: Day 30 fluoride release rates. Error bars indicate standard error.

4.3.9 Day 90 Fluoride Release Rates

None of the materials (Assure™, Quick Cure™ or Transbond™ XT) had detectable fluoride release rates on day 90, making all groups statistically similar. Descriptive statistics of mean fluoride release rates and standard errors are found in Table 32 and Figure 56.

Table 32: Day 90 fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F$^-$/cm^2/day)	SE (μg F$^-$/cm^2/day)
90	Assure™	10	ND	ND
90	Quick Cure™	10	ND	ND
90	Transbond™ XT	10	ND	ND



Columns with similar asterisks are statistically similar ($p>0.05$)

Figure 56: Day 90 fluoride release rates. Error bars indicate standard error.

4.3.10 Day 180 Fluoride Release Rates

None of the materials (Assure™, Quick Cure™ or Transbond™ XT) had detectable fluoride release rates on day 90, making all groups statistically similar. Descriptive statistics of mean fluoride release rates and standard errors are found in Table 33 and Figure 57.

Table 33: Day 180 fluoride release rate descriptive statistics

Day	Adhesive	n	Mean Fluoride Release (μg F$^-$/cm^2/day)	SE (μg F$^-$/cm^2/day)
180	Assure™	10	ND	ND
180	Quick Cure™	10	ND	ND
180	Transbond™ XT	10	ND	ND

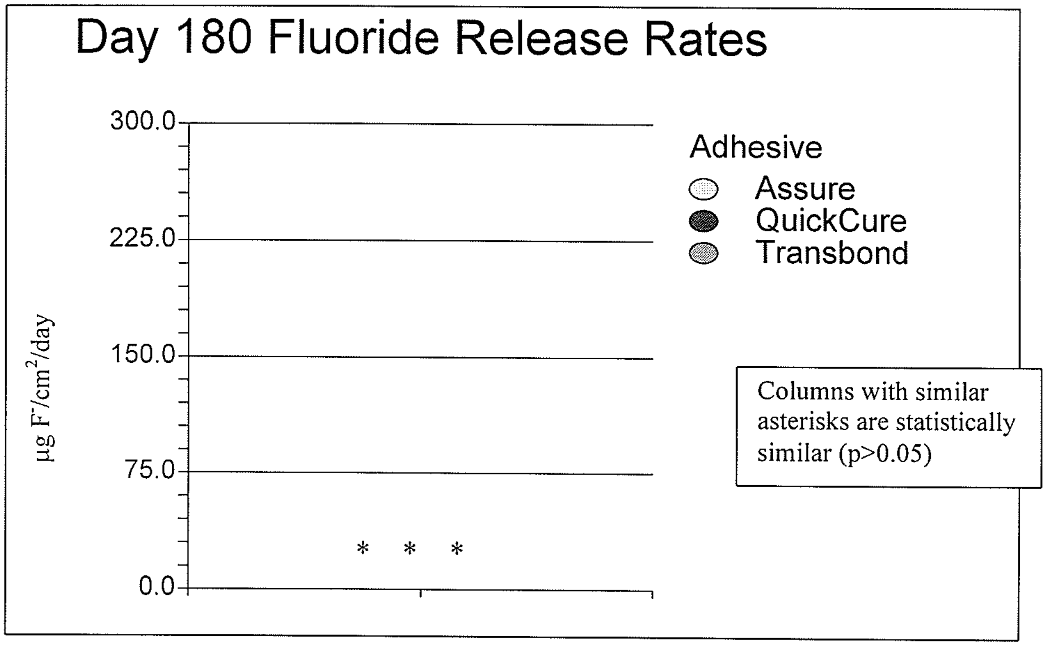


Figure 57: Day 180 fluoride release rates. Error bars indicate standard error.

Chapter 5

Discussion

5.1 Long-Term Fluoride Release

Many analyses of different materials for up to 3 to 6 month durations (Cooley *et al.*, 1989; Wiltshire and Janse van Rensburg, 1995; Young *et al.*, 1996; Monteith *et al.*, 1998; McNeill *et al.*, 2001) have shown that fluoride-releasing bonding materials have an initial releasing "burst effect" in the first 24 hours. This reaches stable levels by the second week (Wiltshire and Janse van Rensburg, 1995; Ashcraft *et al.*, 1997, McNeill *et al.*, 2001), although fluoride release over a comparable term of orthodontic treatment times (e.g. 2 to 3 years) requires further evaluation.

The current investigation was the continuation of a previous 6-month study (McNeill *et al.*, 2001), where the fluoride release rates (in μg F^-/cm^2/day) in distilled water at day 183 were reported as follows: Fuji Ortho™ LC (3.8 ± 1.46), Assure™ (3.1 ± 1.01), Python™ (2.6 ± 1.02) and Transbond™ XT (0.1 ± 0.03) (McNeill *et al.*, 2001). These values were surprisingly lower than the release rates (in μg F^-/cm^2/day) found at the day 546 measurement of the current study for the respective materials: Fuji Ortho™ LC (11.04 ± 0.27), Assure™ (7.68 ± 0.65), Python™ (8.09 ± 0.21) and Transbond™ XT (non-detectable). However, when McNeill *et al.* (2001) measured the fluoride release rate from Assure™ after one year, the fluoride release rate had increased to 10.8 ± 0.77 μg F^-/cm^2/day, a value which was higher than the day 546 measurement in the current study. McNeill (2000) hypothesized that long-term storage in a small volume of water for 6 months resulted in fluoride diffusion from the center of the matrix to the periphery, which created a constant fluoride concentration throughout the sample. It is likely that a similar phenomenon occurred in the present study with a 6-month storage prior to the first measurement.

Other studies have shown long-term fluctuations in fluoride release rates. Temin and Csuros (1988) studied the long-term fluoride release from a fluoridated composite restorative material. Using discs 1.75 x 20 mm in deionized water, they reported a fluoride release rate of 0.35 μg F^-/cm^2/day at day 246, 0.20 μg F^-/cm^2/day at day 410 and 0.19 μg F^-/cm^2/day at day 1591. As in the current study, Temin and Csuros (1988) showed the long-term fluoride release rates fluctuated with time. Wiltshire and Janse van Rensburg (1995) measured the fluoride release rate from FluorEver OBA, a light-cured orthodontic adhesive, using sample sizes (0.94 cm^2) and immersion conditions identical to those used in this study. They found that the release rate fluctuated between 0.35 and 0.5 μg F^-/cm^2/day from week 17 to week 85, with a final measurement of 0.508 μg F^-/cm^2/day at 21.5 months. This is lower than the rates found for any of the fluoride-releasing materials at any time in this study (Assure™, Python™ and Fuji Ortho™ LC), the lowest of which was Assure™ on day 730 (1.04 ± 0.14 μg F^-/cm^2/day). Grobler et al. (1998) found a significant increase in fluoride release rates for several materials from day

60 to day 200. The changes in fluoride release rates (in μg $F^-/cm^2/day$) were as follows: Advance hybrid increased from 0.20 to 0.51, Fuji II LC increased from 0.14 to 0.34, Vitremer increased from 0.12 to 0.26 and Dyract® increased from 0.05 to 0.17.

Fluctuations in fluoride release rates seem to occur with long time periods between measurements, possibly reflecting two fluoride elution processes (Grobler *et al.*, 1998; Tay and Braden, 1988). There is an initial rapid surface process with high and rapid fluoride release that equilibrates after a time, followed by a slow bulk diffusion process that continues for at least 2.5 years (Tay and Braden, 1988). Grobler *et al.* (1998) felt that fluctuations in fluoride release reported in their study were probably due to the time of exposure to water and the diffusion of water into the materials, resulting in the release of fluoride from the bulk of the materials. This slow bulk diffusion may also explain the long-term fluoride release pattern seen in the present study.

In the present study, fluoride was released from Fuji Ortho™ LC, Assure™ and Python™ on days 546, 613, 730, 821 and 913. Transbond™ XT never released sufficient fluoride to meet the detection threshold of the fluoride ion-specific electrode (i.e. less than 0.1 μg $F^-/cm^2/day$). At all time points Fuji Ortho™ LC had significantly greater fluoride release rates than the other materials ($p<0.0001$), followed in order of magnitude by Python™ > Assure™ > Transbond™ XT. These results are supported by those of Monteith *et al.* (1999) who found that the amount of fluoride released by a resin-modified glass-ionomer (Vitremer®) was greater than that from Dyract® Ortho (a polyacid-modified composite) using three different models. Monteith *et al.* (1999) found the mean cumulative concentration of fluoride released from Vitremer® was: unvarnished discs 3 mm in diameter and 1.5 mm in height (25.69 ± 1.52 ppm), varnished discs with half the surface area (18.99 ± 0.83 ppm), and tooth-bracket model (8.92 ± 2.80 ppm). By contrast, the mean cumulative concentration of fluoride released from Dyract® Ortho was: unvarnished discs (6.42 ± 1.00 ppm), varnished discs (5.19 ± 0.83 ppm) and tooth-bracket model (1.48 ± 0.57 ppm) (Monteith *et al.*, 1999). Vermeersch *et al.* (2001) also found that polyacid-modified composite resin materials released less fluoride than resin-modified glass-ionomer cements. Fuji II LC (a resin-modified glass-ionomer cement) had a mean cumulative fluoride release rate of 0.62 ± 0.13 μg/mm^2 at 7 days and 1.86 ± 0.38 μg/mm^2 at 91 days, Vitremer® (a resin-modified glass-ionomer cement) had a mean cumulative fluoride release rate of 0.43 ± 0.13 μg/mm^2 on day 7 and 1.00 ± 0.24 μg/mm^2 on day 91, and Dyract® (a polyacid-modified composite resin) had a mean cumulative fluoride release rate of 0.08 ± 0.03 μg/mm^2 on day 7 and 0.41 ± 0.10 μg/mm^2 on day 91. These results therefore indicate that the fluoride release rate for the resin-modified glass-ionomer cement (Fuji Ortho™ LC) was greater than those of the polyacid-modified composite resins (Assure™ and Python™).

The fluoride release rate for Python™ was significantly greater than that of Assure™ on days 730, 821 and 913 ($p<0.0001$). All fluoride-releasing materials showed a decrease in release rates until day 730 (Python™ and Assure™) or 821 (Fuji Ortho™ LC), followed by an increase until day 913. The reason for the increase in fluoride release rates at day 913 remains unclear. On days 730 and 821 Assure™ had fluoride release rates of 1.04 ± 0.14

and 1.21 ± 0.23 μg F$^-$/cm^2/day. These were statistically similar to the control material Transbond™ XT ($P>0.05$), yet offer clinically significant enamel protection. Rawls (1987 and 1995) states that to inhibit caries initiation in sound enamel in the immediate vicinity of a resin-based dental material, fluoride release should be in the range of 0.65 to 1.3 μg F$^-$/cm^2/day. All fluoride-releasing materials (Fuji Ortho™ LC, Assure™ and Python™) had long-term fluoride release rates at or above this level throughout the experiment, and so may be considered cariostatic.

Several studies have reported long-term fluoride release from various materials, although few have reported on fluoride-releasing orthodontic bonding materials. Fox (1998) studied fluoride release from a polyacid-modified composite resin (Direct®) and a glass ionomer cement (Ketac-Cem®), both of which are non-orthodontic bonding materials. The sample size used was 10 mm x 10 mm x 1 mm, resulting in a surface area of 2.4 cm^2 (for comparison, the results of the study have been converted from μg/day to μg/cm^2/day). Fox (1998) found the fluoride release rate for Direct® on day 2 was 4.1 μg/cm^2/day, which dropped to 0.1 μg/cm^2/day by 10 weeks and stayed at that level up to 20 weeks. Ketac-Cem® had higher fluoride release rates on day 2 (36.7 μg/cm^2/day), but dropped below 0.1 μg/cm^2/day at 6 weeks and remained below through week 20. Fox (1998) found essentially no long-term fluoride release for Direct® and Ketac-Cem® as compared to the materials in the present study.

Trimpeneers *et al.* (1998) also studied fluoride release from orthodontic bonding resins over a long-term period of 560 days. Utilizing samples with dimensions 13 mm diameter x 1.2 mm thickness, they studied fluoride release rates from Light-Bond, Rely.a.Bond, Orthon, FluorEver and Ketac-Cem®. Direct comparison of these results is difficult because fluoride release rates were reported in mmol/L/day. Nevertheless, FluorEver and Ketac-Cem® had a continuous, slow decline in fluoride release over the evaluation period. Fluoride release from Orthon, however, increased after a period of time to a constant higher level than those of Ketac-Cem® and FluorEver. Again, variability in fluoride release patterns was attributed to differencet kinetic processes (Trimpeneers *et al.*, 1998).

5.2 Fluoride Re-Release Pattern

As discussed in section 5.1, fluoride-releasing materials show a "burst-effect" fluoride release pattern (i.e. the greatest amount of fluoride is released within the first few days of testing) (Wiltshire and Janse van Rensburg, 1995; Ashcraft *et al.*, 1997). With a rapid decline to much lower levels, it is important to examine the usefulness of these materials as fluoride "reservoirs" during the average orthodontic treatment time of two to three years by determining the fluoride re-release pattern after exposure to additional fluoride. Fluoride exposure often occurs clinically, such as when patients receive topical fluoride applications during treatment or ingest fluoride-containing drinks or food. In agreement with previous studies (Takahashi *et al.*, 1993; Young *et al.*, 1996; McNeill *et al.*, 2001), this experiment showed a similar 'burst-effect' fluoride re-release pattern following exposure of aged samples to 2% sodium fluoride (NaF) gel. The fluoride re-release rates (in μg F^-/cm^2/day) for Fuji Ortho™ LC (92.34 ± 1.48), Assure™ (63.40 ± 4.68), and Python™ (36.60 ± 5.19) were much higher than the values reported by McNeill *et al.* (2001) for the same samples 12 months earlier (at day 183): Fuji Ortho™ LC (3.8 ± 1.46), Assure™ (3.1 ± 1.01), Python™ (2.6 ± 1.02) and Transbond™ XT (0.1 ± 0.03).

The fluoride release rates were significantly greer 24 hours post-exposure (day 546) compared to subsequent measurements ($p<0.0001$). The rapid decrease in fluoride release after one day supports the findings of De Witte *et al.* (2000) who investigated the fluoride release profiles of mature restorative resin-modified glass-ionomer and conventional glass-ionomer cements after fluoride application. They found that conventional and resin-modified GICs could be charged with fluoride (2% NaF for 1 hour) after maturing for 21 days, and this release rate lasted for only a few days. They felt that the short-term release process seen after fluoridation was due to the kinetic processes involved. More specifically, some fluoride is free to move into the cement and is subsequently easily released by simple diffusion through the matrix, while other fluoride penetrates the GIC upon fluoridation and reacts with aluminum, calcium or other bivalent metal ions of the matrix, forming matrix-bound fluoride. The unbound fluoride would account for the short-term elution, while the matrix-bound fluoride could only be released following decomplexation and might be related to the long-term elution process. On subsequent fluoridations they found that the short-term process explained the amount of fluoride released. Less fluoride could become matrix bound because many, if not all, of the metal ions were complexed, allowing more of the fluoride to remain free within the matrix. Consequently, the short-term fluoride release would be more prominent with each fluoride exposure (De Witte *et al.*, 2000).

Young *et al.* (1996) studied fluoride release and re-release from two fluoride-containing orthodontic adhesives (Saga Bond and VP 862), a polyacid modified composite (Tetric) and a glass-ionomer cement material (Ketac Fil®). They found all materials had greatly increased fluoride release after exposure to 1000 ppm NaF solution, followed by a return to pre-exposure levels within 2-3 days. This pattern was similar to the present study, with the leveling-off of fluoride release rates by the third day (day 548). Young *et al.* (1996) also reported an increase in 'base-line' fluoride release from Ketac-Fil® with repeated fluoride exposures. The remaining materials, however, showed a trend of decreasing fluoride release in the initial 24-hour follow-up period with repeated exposures. This trend might have changed with a longer follow-up period (i.e. fluoride exposures occurred on days 33, 40 and 46). They reasoned that there was a possible reduction in 'constant' fluoride release from the materials or the surface became saturated with fluoride following several exposures (Young *et al.*, 1996).

On day 546, Fuji Ortho™ LC had the highest fluoride release rate (92.34 ± 1.48 μg F^-/cm^2/day), followed by Assure™ (63.40 ± 4.68 μg F^-/cm^2/day), Python™ (36.60 ± 5.19 μg F^-/cm^2/day) and Transbond™ XT (5.94 ± 1.24 μg F^-/cm^2/day). On all subsequent days the fluoride release rates (in decreasing order) were as follows: Fuji Ortho™ LC > Python™ > Assure™ > Transbond™ XT. These results are consistent with those reported by Yip and Smales (1999), who studied fluoride release and uptake by aged resin-modified glass-ionomers (Fuji II LC, Photac-Fil and Vitremer) and a polyacid modified resin composite (Dyract). Using samples 3 mm in diameter x 2.7 mm in height submerged in 2 mL of deionized water, fluoride release was shown to be higher for resin-modified glass-ionomer cements following fluoride exposure relative to the polyacid-modified resin composite. At 2 hours following exposure to NaF, the concentration of fluoride released by the samples was as follows: Photac-Fil (2.54 ppm) > Fuji II LC (2.28 ppm) > Vitremer (2.10 ppm) > Dyract (0.56 ppm). At 21 days following exposure to NaF, the order was slightly different, but the resin-modified glass-ionomers still had the greatest concentration of fluoride release: Photac-Fil (0.54 ppm) > Vitremer (0.23 ppm) > Fuji II LC (0.20 ppm) > Dyract (0.20 ppm).

On days 548, 552, 575, 637, 730, 821 and 913 no statistical difference was apparent in release rates (in μg F^-/cm^2/day) between Assure™ (2.90 ± 0.88 on day 548), Python™ (5.85 ± 0.36 on day 548) and the control material Transbond™ XT (0.043 ± 0.043 on day 548). However, as mentioned in section 5.1, the difference may be clinically significant, based on experiments determining the minimum fluoride level that offers cariostatic protection. Again using Rawls' (1995) values for significant fluoride release rates (0.65 to 1.3 μg F^-/cm^2/day) needed to inhibit caries after fluoride exposure; all fluoride-releasing materials (Fuji Ortho™ LC, Assure™ and Python™) met or exceeded this standard in the present study.

Creanor *et al.* (1994) studied fluoride uptake and re-release of such glass ionomer cements as Ketac Fil®, Chemfil Superior, Fuji II LC, Aquacem and Vitrebond. They immersed samples in 1 L of deionized water for 60 days to leach fluoride out of the materials and divided them into control and experimental groups. The experimental samples were then exposed to 1000 ppm F^- solution daily for 20 days, when they found that the exposed samples released more ionic fluoride than the controls at all time points over the 20 days. This indicated that all five types of glass ionomer cements imbibe and re-release fluoride.

The fluoride re-release patterns seen in this experiment and other studies may be due to two different mechanisms, including: I) surface retention of fluoride and II) diffusion of fluoride into the matrix of the material. Surface retention of fluoride is supported by the results using non-fluoridated control materials. In the present study it was found that Transbond™ XT had greater fluoride release in the initial 24 hours post-exposure (5.94 ± 1.24 μg F^-/cm^2/day) than at any time following, even though these differences were not significant ($p>0.05$). Takahashi *et al.* (1993) found fluoride release of 0.06 ± 0.01 mmol/L in the first week post-exposure, compared with 0.01 ± 0.01 mmol/L pre-exposure from a composite resin (Prisma APH). Young *et al.* (1996) reported that Tetric (a polyacid-modified composite) had a fluoride release of 8.5 ± 2.62 mg/cm^2 24 hours post-exposure, compared with 0.27 ± 0.04 mg/cm^2 at the initial 24 hour measurement. They felt that the increased fluoride release rate for Tetric (a polyacid modified composite) was most likely due to surface-retained fluoride; the most likely explanation for the increased fluoride release from Transbond™ XT following fluoride exposure in this experiment.

Diffusion of fluoride in the matrix material is supported by fluoride re-release rates from fluoride-releasing bonding materials. For example, Takahashi *et al.* (1993) used 6-week-old samples to compare fluoride release following exposure to 2% NaF, 0.2% NaF, 0.02% NaF and distilled water (no NaF). They found that the 0.02% exposed group did not release more fluoride than controls immersed in distilled water, while the 2% and 0.2% NaF exposed samples released extra fluoride during the 3 weeks post-exposure. These results illustrate that some fluoride must have diffused into the matrix material, as it could not be accounted for by washout of fluoride ions adsorbed to the surface. It is likely that for the fluoride-releasing materials used in this study, both surface adsorption and matrix diffusion of fluoride from NaF gel resulted in the 'burst-effect' fluoride release pattern - a significant clinical benefit for their use in orthodontics.

5.3 Tooth-Bracket Model

Fluoride release from orthodontic bonding materials may be important only if sufficient to provide a cariostatic benefit. According to Monteith *et al.* (1999), the amount of fluoride varies with the *in vitro* model used. Utilizing a tooth-bracket model would therefore provide valuable insight into the amount of fluoride release *in vivo*. The tooth-bracket model in this study was used to evaluate two materials that are marketed as fluoride releasing (Assure™ and Quick Cure™), by comparing them with a non-fluoride releasing control composite resin (Transbond™ XT). As expected, Transbond™ XT did not release detectable levels of fluoride at any point in the experiment. Assure™ released detectable levels of fluoride on days 1, 3, 7 and 30, with the fluoride release rate on day 1 being significantly greater than on subsequent days ($p<0.0001$). On days 3, 7 and 30 the mean fluoride release rates were not significantly different from the control ($p>0.05$). This may be clinically significant since they still exceeded the caries inhibitory fluoride release rates of 0.65 to 1.3 μg F^-/cm^2/day. However, the variation in fluoride release rates between individual samples indicates that not all orthodontic brackets bonded with fluoride-releasing bonding materials may be similarly protective. Quick Cure™, meanwhile, released detectable levels only on day 1 (and this was only from 2 samples). The fluoride release rates for Quick Cure™ were statistically similar at all time periods ($p>0.05$). Since there are no other independent reports of fluoride release rates for Quick Cure™ using a tooth-bracket model, it is assumed that minimal fluoride is released from this material.

There is only one reported study of fluoride release from Assure™ using a tooth-bracket model (Rix *et al.*, 2001), which showed the following release rates: day 1 (89.74 μg F^-/cm^2/day), day 3 (64.10 μg F^-/cm^2/day) and day 7 (13.46 μg F^-/cm^2/day). The reported fluoride release rates in μg F^-/bracket/day up to 1 month are difficult to compare with this study because of differences in units. It is important to note, however, that Assure™ had a release rate of 0 μg F^-/bracket/day on day 28, revealing a similar burst-effect, followed by the trend for fluoride release rates to diminish to non-detectable levels. The current findings show a rate of 3.03 ± 1.65 μg F^-/cm^2/day on day 30 and non-detectable fluoride release on days 90 and 180. Unlike the disc samples, this indicates rebound in fluoride release rate did not occur by 6 months, probably due to the smaller amount of material used. It is possible that all fluoride had diffused out and was released by this point with the minimal amount of bonding material present.

Rix *et al.* (2001) also studied the fluoride release rates (in μg F^-/cm^2/day) for Fuji Ortho™ LC using a tooth-bracket model, and found that they were higher than those reported for Assure™. Fuji Ortho™ LC released 157.05 on day 1, decreasing to 26.92 on day 3 and 20.51 on day 7. It is important to note that for Assure™ and Fuji Ortho™ LC, greater fluoride release rates were reported from the bracketed teeth than from discs of the same materials (Rix *et al.*, 2001), a finding similar to this study, especially for Assure™ on day 1 (236.39 ± 49.14 μg F^-/cm^2/day). Large variation in fluoride release rates for the tooth-bracket samples may also reflect the presence of flash material around the bracket periphery, which again mimics the clinical situation where flash is quite prevalent.

Chan *et al.* (1990) used a tooth-bracket model to investigate fluoride release rates for FluorEver OBA. The reported fluoride release rates (in μg F^-/cm^2/day) as follows: day 1 (~ 700), day 3 (52.6 ± 13.2) and day 43 (10.5 ± 2.6). This was a fairly consistent pattern with Assure™ in this study; however, FluorEver OBA had higher initial rates and a less rapid decline up to approximately one month.

Ashcraft *et al.* (1997) studied fluoride release from three resin-modified glass ionomer cements (Band-Lok, Zionomer and Geristore) using a tooth-bracket model. While comparison of results with the current study is difficult because values were reported in concentration of fluoride release (ppm), the overall pattern of release is important. They found that Bank-Lok released significantly more fluoride than the other materials on each day that fluoride was released. The concentration of fluoride released on day 1 for each material was as follows: Geristore (1.50 ppm), Zionomer (0.36 ppm) and Geristore (0.50 ppm). Both Zionomer and Geristore showed rapid decreases in fluoride ion release after initial cure to near zero ppm on day 7 (Ashcraft *et al.*, 1997). Ghani *et al.* (1994) also used a tooth-bracket model to report fluoride release from orthodontic bonding composites Mirage Dual Cure® and Reliance®. The experimental period only lasted for 8 days, during which the concentration of fluoride released from Mirage Dual Cure® decreased from 0.49 ± 0.09 ppm to 0.13 ± 0.03 ppm, and Reliance® decreased from 0.30 ± 0.01 ppm to 0.13 ± 0.04 ppm (Ghani *et al.*, 1994).

In summary, using two different *in vitro* models, fluoride release was found to be a common phenomenon with Fuji Ortho™ LC, Assure™ and Python™. Consequently, these materials offer a potentially significant cariostatic effect in the clinical situation of bracket bonding.

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

From the present study, the following conclusions can be made:

- Fuji Ortho™ LC had the greatest fluoride release of the materials investigated in this study.
- Fuji Ortho™ LC, Assure™ and Python™ had long-term fluoride-release rates above the range of 0.65 to 1.3 μg F^-/cm^2/day recommended by Rawls (1987 and 1995) to inhibit caries initiation in sound enamel in the immediate vicinity of a resin-based dental material.
- Fuji Ortho™ LC, Assure™ and Python™ all demonstrated a 'burst-effect' pattern of fluoride re-release following exposure to 2% sodium fluoride gel. These materials had fluoride release rates that fell to low, consistent levels that were above the range of 0.65 to 1.3 μg F^-/cm^2/day recommended by Rawls (1987 and 1995). The fluoride uptake and re-release is probably due the processes of surface adsorption and matrix diffusion of fluoride.
- Using a tooth-bracket model, Assure™ was found to be a suitable fluoride-releasing material, as it released clinically significant levels of fluoride up to day

30. Quick Cure™ released fluoride at levels similar to the non-fluoride releasing control Transbond™ XT.

Therefore, the null hypothesis that stated:

1) Samples of resin-modified glass-ionomer (Fuji Ortho™ LC) will not release more fluoride than either polyacid-modified composite resin (Assure™ and Python™) or a non-fluoride-containing composite resin (Transbond™ XT) **is rejected** because Fuji Ortho™ LC had significantly greater fluoride release rates than Python™ or Assure™ at all time points ($p<0.0001$).
2) Samples of resin-modified glass-ionomer (Fuji Ortho™ LC) will not imbibe and re-release more fluoride than either polyacid-modified composite resin (Assure™ and Python™) or a non-fluoride-containing composite resins (Transbond™ XT) **is rejected** because on day 546 Fuji Ortho™ LC released significantly more fluoride than any other material ($p<0.0001$).
3) A tooth-bracket model of either polyacid-modified composite resin (Assure™ and Quick Cure™) will not release more fluoride than a non-fluoride-containing composite resin **is rejected** because Assure™ released significantly more fluoride on day 1 than Quick Cure™ or Transbond™ XT ($p<0.0001$).

6.2 Recommendations

From investigation of the literature and results of this study, the following recommendations are made:

- When bonding orthodontic attachments, materials that release fluoride should be used because they are likely to provide protection from white spot formation.
- Fuji Ortho™ LC, Assure™ and Python™ have sufficient long-term fluoride release rates to reduce white spot formation and are all recommended as suitable orthodontic bonding materials.
- The use of Quick Cure™ as a fluoride-releasing bonding material cannot be recommended because detectable fluoride release rates (using a tooth-bracket model) were found only on day 1, and these rates were not significantly different from any subsequent measurement which had non-detectable fluoride release rates.

6.3 Future Research

Future research of fluoride releasing materials should involve *in vivo* clinical trials to assess any anti-cariogenic effect and validate the reliability of *in vitro* studies.

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Appendix 1: Long-Term Fluoride Release Samples

Adhesive	Sample #	Day	µgF$^-$/cm^2/day
Transbond XT	1	546	0
Transbond XT	1	637	0
Transbond XT	1	730	0
Transbond XT	1	821	0
Transbond XT	1	913	0
Transbond XT	2	546	0
Transbond XT	2	637	0
Transbond XT	2	730	0
Transbond XT	2	821	0
Transbond XT	2	913	0
Transbond XT	3	546	0
Transbond XT	3	637	0
Transbond XT	3	730	0
Transbond XT	3	821	0
Transbond XT	3	913	0
Transbond XT	4	546	0
Transbond XT	4	637	0
Transbond XT	4	730	0
Transbond XT	4	821	0
Transbond XT	4	913	0
Transbond XT	5	546	0
Transbond XT	5	637	0
Transbond XT	5	730	0
Transbond XT	5	821	0
Transbond XT	5	913	0
Python	1	546	8.72
Python	1	637	5.96
Python	1	730	4.57
Python	1	821	6.70
Python	1	913	7.13
Python	2	546	7.98
Python	2	637	4.68
Python	2	730	4.04
Python	2	821	4.89
Python	2	913	6.17
Python	3	546	7.66
Python	3	637	4.89
Python	3	730	4.04
Python	3	821	5.96
Python	3	913	6.60
Python	4	546	7.66
Python	4	637	6.60
Python	4	730	4.57
Python	4	821	6.49
Python	4	913	6.60
Python	5	546	8.40
Python	5	637	6.81
Python	5	730	5.11
Python	5	821	6.91
Python	5	913	7.34
Assure	1	546	8.40
Assure	1	637	3.83
Assure	1	730	0.87
Assure	1	821	0.96
Assure	1	913	4.68
Assure	2	546	7.34
Assure	2	637	7.34
Assure	2	730	1.60
Assure	2	821	1.06
Assure	2	913	4.89
Assure	3	546	8.30
Assure	3	637	2.77
Assure	3	730	0.85
Assure	3	821	0.90
Assure	3	913	5.53
Assure	4	546	9.04
Assure	4	637	5.32
Assure	4	730	1.01
Assure	4	821	1.01
Assure	4	913	4.68
Assure	5	546	5.32
Assure	5	637	3.83
Assure	5	730	0.85
Assure	5	821	2.13
Assure	5	913	4.36
Fuji Ortho LC	1	546	10.53
Fuji Ortho LC	1	637	10.32
Fuji Ortho LC	1	730	10.21
Fuji Ortho LC	1	821	10.05
Fuji Ortho LC	1	913	10.43
Fuji Ortho LC	2	546	11.70
Fuji Ortho LC	2	637	10.43
Fuji Ortho LC	2	730	10.11
Fuji Ortho LC	2	821	10.11
Fuji Ortho LC	2	913	10.37
Fuji Ortho LC	3	546	11.70
Fuji Ortho LC	3	637	10.53

Adhesive	Sample #	Day	$\mu gF^{-}/cm^{2}/day$
Fuji Ortho LC	3	730	10.32
Fuji Ortho LC	3	821	10.21
Fuji Ortho LC	3	913	10.27
Fuji Ortho LC	4	546	10.64
Fuji Ortho LC	4	637	10.53
Fuji Ortho LC	4	730	10.32
Fuji Ortho LC	4	821	10.32
Fuji Ortho LC	4	913	10.27
Fuji Ortho LC	5	546	10.64
Fuji Ortho LC	5	637	10.43
Fuji Ortho LC	5	730	9.95
Fuji Ortho LC	5	821	10.05
Fuji Ortho LC	5	913	10.32

Appendix 2: Fluoride Re-release Samples

Adhesive	Sample #	Day	$\mu gF^-/cm^2/day$
Transbond XT	1	546	6.28
Transbond XT	1	548	0.21
Transbond XT	1	552	0
Transbond XT	1	575	0.11
Transbond XT	1	637	0.13
Transbond XT	1	730	0
Transbond XT	1	821	0
Transbond XT	1	913	0
Transbond XT	2	546	8.72
Transbond XT	2	548	0
Transbond XT	2	552	0
Transbond XT	2	575	0
Transbond XT	2	637	0
Transbond XT	2	730	0
Transbond XT	2	821	0
Transbond XT	2	913	0
Transbond XT	3	546	8.30
Transbond XT	3	548	0
Transbond XT	3	552	0
Transbond XT	3	575	0
Transbond XT	3	637	0
Transbond XT	3	730	0
Transbond XT	3	821	0
Transbond XT	3	913	0
Transbond XT	4	546	2.13
Transbond XT	4	548	0
Transbond XT	4	552	0
Transbond XT	4	575	0
Transbond XT	4	637	0
Transbond XT	4	730	0
Transbond XT	4	821	0
Transbond XT	4	913	0
Transbond XT	5	546	4.26
Transbond XT	5	548	0
Transbond XT	5	552	0
Transbond XT	5	575	0
Transbond XT	5	637	0
Transbond XT	5	730	0
Transbond XT	5	821	0
Transbond XT	5	913	0
Python	1	546	40.43
Python	1	548	6.28
Python	1	552	2.87
Python	1	575	4.89
Python	1	637	5.53
Python	1	730	5.53
Python	1	821	5.32
Python	1	913	6.38
Python	2	546	19.15
Python	2	548	4.68
Python	2	552	0.96
Python	2	575	2.55
Python	2	637	5.32
Python	2	730	5.53
Python	2	821	6.92
Python	2	913	7.34
Python	3	546	51.06
Python	3	548	5.32
Python	3	552	1.60
Python	3	575	3.83
Python	3	637	6.60
Python	3	730	5.85
Python	3	821	7.66
Python	3	913	7.66
Python	4	546	34.04
Python	4	548	6.50
Python	4	552	1.60
Python	4	575	3.30
Python	4	637	5.74
Python	4	730	5.32
Python	4	821	7.02
Python	4	913	7.13
Python	5	546	38.30
Python	5	548	6.49
Python	5	552	2.34
Python	5	575	3.83
Python	5	637	5.74
Python	5	730	4.79
Python	5	821	6.49
Python	5	913	7.66
Assure	1	546	70.21
Assure	1	548	3.62
Assure	1	552	0.85
Assure	1	575	0.83
Assure	1	637	4.68
Assure	1	730	1.91

Adhesive	Sample #	Day	$\mu gF^-/cm^2/day$
Assure	1	821	1.49
Assure	1	913	4.36
Assure	2	546	76.60
Assure	2	548	3.83
Assure	2	552	0.64
Assure	2	575	1.49
Assure	2	637	4.04
Assure	2	730	1.60
Assure	2	821	0.90
Assure	2	913	5.74
Assure	3	546	51.06
Assure	3	548	0.81
Assure	3	552	0.43
Assure	3	575	0.69
Assure	3	637	3.83
Assure	3	730	0.64
Assure	3	821	0.85
Assure	3	913	3.40
Assure	4	546	55.32
Assure	4	548	0.91
Assure	4	552	0.53
Assure	4	575	0.62
Assure	4	637	2.77
Assure	4	730	0.85
Assure	4	821	1.811
Assure	4	913	5.11
Assure	5	546	63.83
Assure	5	548	5.32
Assure	5	552	0.85
Assure	5	575	0.69
Assure	5	637	1.03
Assure	5	730	1.38
Assure	5	821	0.96
Assure	5	913	3.40
Fuji Ortho LC	1	546	89.36
Fuji Ortho LC	1	548	10.21
Fuji Ortho LC	1	552	9.47
Fuji Ortho LC	1	575	10.11
Fuji Ortho LC	1	637	10.21
Fuji Ortho LC	1	730	10.21
Fuji Ortho LC	1	821	10.11
Fuji Ortho LC	1	913	10.37
Fuji Ortho LC	2	546	88.30
Fuji Ortho LC	2	548	10.21
Fuji Ortho LC	2	552	9.15
Fuji Ortho LC	2	575	9.79
Fuji Ortho LC	2	637	9.89
Fuji Ortho LC	2	730	10.00
Fuji Ortho LC	2	821	10.10
Fuji Ortho LC	2	913	10.27
Fuji Ortho LC	3	546	94.68
Fuji Ortho LC	3	548	10.64
Fuji Ortho LC	3	552	9.68
Fuji Ortho LC	3	575	10.11
Fuji Ortho LC	3	637	10.16
Fuji Ortho LC	3	730	10.11
Fuji Ortho LC	3	821	10.27
Fuji Ortho LC	3	913	10.32
Fuji Ortho LC	4	546	93.62
Fuji Ortho LC	4	548	10.53
Fuji Ortho LC	4	552	9.68
Fuji Ortho LC	4	575	10.21
Fuji Ortho LC	4	637	10.27
Fuji Ortho LC	4	730	10.00
Fuji Ortho LC	4	821	10.32
Fuji Ortho LC	4	913	10.37
Fuji Ortho LC	5	546	95.74
Fuji Ortho LC	5	548	21.28
Fuji Ortho LC	5	552	9.57
Fuji Ortho LC	5	575	10.11
Fuji Ortho LC	5	637	10.16
Fuji Ortho LC	5	730	10.00
Fuji Ortho LC	5	821	10.21
Fuji Ortho LC	5	913	10.32

Appendix 3: Tooth-Bracket Samples

Adhesive	Sample #	Day	$\mu gF^-/cm^2/day$
Transbond XT	1	1	0
Transbond XT	1	3	0
Transbond XT	1	7	0
Transbond XT	1	30	0
Transbond XT	1	90	0
Transbond XT	1	180	0
Transbond XT	2	1	0
Transbond XT	2	3	0
Transbond XT	2	7	0
Transbond XT	2	30	0
Transbond XT	2	90	0
Transbond XT	2	180	0
Transbond XT	3	1	0
Transbond XT	3	3	0
Transbond XT	3	7	0
Transbond XT	3	30	0
Transbond XT	3	90	0
Transbond XT	3	180	0
Transbond XT	4	1	0
Transbond XT	4	3	0
Transbond XT	4	7	0
Transbond XT	4	30	0
Transbond XT	4	90	0
Transbond XT	4	180	0
Transbond XT	5	1	0
Transbond XT	5	3	0
Transbond XT	5	7	0
Transbond XT	5	30	0
Transbond XT	5	90	0
Transbond XT	5	180	0
Transbond XT	6	1	0
Transbond XT	6	3	0
Transbond XT	6	7	0
Transbond XT	6	30	0
Transbond XT	6	90	0
Transbond XT	6	180	0
Transbond XT	7	1	0
Transbond XT	7	3	0
Transbond XT	7	7	0
Transbond XT	7	30	0
Transbond XT	7	90	0
Transbond XT	7	180	0
Transbond XT	8	1	0

/day Adhesive	Sample #	Day	$\mu gF^-/cm^2/day$
Transbond XT	8	3	0
Transbond XT	8	7	0
Transbond XT	8	30	0
Transbond XT	8	90	0
Transbond XT	8	180	0
Transbond XT	9	1	0
Transbond XT	9	3	0
Transbond XT	9	7	0
Transbond XT	9	30	0
Transbond XT	9	90	0
Transbond XT	9	180	0
Transbond XT	10	1	0
Transbond XT	10	3	0
Transbond XT	10	7	0
Transbond XT	10	30	0
Transbond XT	10	90	0
Transbond XT	10	180	0
Quick Cure	1	1	0
Quick Cure	1	3	0
Quick Cure	1	7	0
Quick Cure	1	30	0
Quick Cure	1	90	0
Quick Cure	1	180	0
Quick Cure	2	1	0
Quick Cure	2	3	0
Quick Cure	2	7	0
Quick Cure	2	30	0
Quick Cure	2	90	0
Quick Cure	2	180	0
Quick Cure	3	1	0
Quick Cure	3	3	0
Quick Cure	3	7	0
Quick Cure	3	30	0
Quick Cure	3	90	0
Quick Cure	3	180	0
Quick Cure	4	1	0
Quick Cure	4	3	0
Quick Cure	4	7	0
Quick Cure	4	30	0
Quick Cure	4	90	0
Quick Cure	4	180	0
Quick Cure	5	1	0
Quick Cure	5	3	0

Adhesive	Sample #	Day	µgF$^-$/cm^2/day
Quick Cure	5	7	0
Quick Cure	5	30	0
Quick Cure	5	90	0
Quick Cure	5	180	0
Quick Cure	6	1	0
Quick Cure	6	3	0
Quick Cure	6	7	0
Quick Cure	6	30	0
Quick Cure	6	90	0
Quick Cure	6	180	0
Quick Cure	7	1	53.00
Quick Cure	7	3	0
Quick Cure	7	7	0
Quick Cure	7	30	0
Quick Cure	7	90	0
Quick Cure	7	180	0
Quick Cure	8	1	0
Quick Cure	8	3	0
Quick Cure	8	7	0
Quick Cure	8	30	0
Quick Cure	8	90	0
Quick Cure	8	180	0
Quick Cure	9	1	0
Quick Cure	9	3	0
Quick Cure	9	7	0
Quick Cure	9	30	0
Quick Cure	9	90	0
Quick Cure	9	180	0
Quick Cure	10	1	51.50
Quick Cure	10	3	0
Quick Cure	10	7	0
Quick Cure	10	30	0
Quick Cure	10	90	0
Quick Cure	10	180	0
Assure	1	1	152.81
Assure	1	3	25.88
Assure	1	7	2.26
Assure	1	30	15.37
Assure	1	90	0
Assure	1	180	0
Assure	2	1	246.10
Assure	2	3	84.85
Assure	2	7	72.18
Assure	2	30	9.18
Assure	2	90	0
Assure	2	180	0

Adhesive	Sample #	Day	µgF$^-$/cm^2/day
Assure	3	1	137.19
Assure	3	3	19.71
Assure	3	7	1.11
Assure	3	30	0
Assure	3	90	0
Assure	3	180	0
Assure	4	1	599.41
Assure	4	3	42.21
Assure	4	7	0
Assure	4	30	0
Assure	4	90	0
Assure	4	180	0
Assure	5	1	394.26
Assure	5	3	43.06
Assure	5	7	11.95
Assure	5	30	0
Assure	5	90	0
Assure	5	180	0
Assure	6	1	185.73
Assure	6	3	60.79
Assure	6	7	19.20
Assure	6	30	0
Assure	6	90	0
Assure	6	180	0
Assure	7	1	134.23
Assure	7	3	18.40
Assure	7	7	5.15
Assure	7	30	2.22
Assure	7	90	0
Assure	7	180	0
Assure	8	1	124.53
Assure	8	3	22.54
Assure	8	7	2.49
Assure	8	30	0
Assure	8	90	0
Assure	8	180	0
Assure	9	1	108.91
Assure	9	3	15.75
Assure	9	7	0
Assure	9	30	0
Assure	9	90	0
Assure	9	180	0
Assure	10	1	280.71
Assure	10	3	82.70
Assure	10	7	30.60
Assure	10	30	3.55

Adhesive	Sample #	Day	$\mu gF^{-}/cm^{2}/day$
Assure	10	90	0
Assure	10	180	0